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**(54) Tubular air cathode, method of fabricating**

(57) An elongate, generally tubular, air depolarized electrochemical cell (10) comprising a cathode (14), including an air cathode assembly (26), extending about the tubular circumference, and along the tubular length, of the cell (10), an anode (12), a separator (18) between the anode (12) and the cathode (14), electrolyte, a top closure member (177, 200), and a bottom closure member (114, 202). The cathode assembly (26) is fixedly held, by a friction fit, in a slot (116) at the bottom of the cell. The slot can be developed, for example, by inner (110) and outer (114) walls of a cathode can (28), by inner (226) and outer (224) walls of a bottom closure member (202), or by an outer wall (114) of a cathode can (28) and an opposing outer wall of a plug (128) on the interior of the cell. Preferably, bottom closure structure of the cell (10) and receives a bottom edge portion (44) of the cathode current collector (32), and makes electrical contact with the bottom edge portion (44), preferably at an inner surface (60) of the cathode current collector. A diffusion member (36) of the cathode assembly (26) is preferably compressed as a seal, at the bottom of the cell (10), between an outer side wall (39) of the cell and the remainder of the cathode assembly (26). The diffusion member (36) is also used at least as an assist in sealing the cell (10) against electrolyte leakage from the anode cavity (137) and past the cathode assembly (26).

The current collector (32) can be cylindrical and can be free from longitudinal jointing, or can have a longitu-

dinal joint (54), preferably free from overlap of the side wall. The current collector (32) can comprise an impermeate edge region at the top (42) and/or bottom (44), left (48) and/or right (46) edge. The perforations (56) define an open fraction of the wall, of about 45 to about 70 percent. Typical cathode assemblies (26) have air diffusion member (36) on the outer surface of the cathode assembly (26). Such air diffusion member (36) typically has thickness of about 0.0025 to 0.005 inch (about .06 to about .13 mm.), and comprises a reduced thickness endless wrap extending at least 1.5 times, preferably 2 times, or 3 times, about the current collector (32), discouraging transfer of moisture vapor into or out of a cell, discouraging leakage, and controlling air diffusion rate. The diffusion member (36) extends beyond the top edge (42) of the current collector, and is folded in and down about the top edge (42) and inner surface (60) of the cathode assembly (26). The cathode current collector (32) can be mounted on a mandrel (93), the carbon sheet (80) passing through a nip defined between (i) support structure (192) having greater arc radius than the mandrel (93) and (ii) the mandrel (93), and applying force at the nip to consolidate the carbon (80) onto the side wall (58), passing air diffusion material (36) through the nip, and applying force to consolidate the air diffusion material (36) onto the carbon (80). The invention contemplates fabricating an air cathode assembly (26) comprising mounting the current collector (32) on a mandrel (93), defining an arc having a radius smaller

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## Description

## BACKGROUND

- 5 [0001] This invention relates to air depolarized electrochemical cells. This invention is related specifically to metal-air, air depolarized electrochemical cells, illustrated herein both as elongate cylindrical cells and as button-shaped cells. Elongate cells are described herein with respect to cells having the size generally known as "AA." Button cells are commercially produced in smaller sizes having lesser height-to-diameter ratios, and are generally directed toward use in hearing aids, and small computer cells. Such button cells generally feature overall contained cell volume of less than 2 cm<sup>3</sup>, and for the hearing aid cells less than 1 cm<sup>3</sup>.
- 10 [0002] The advantages of air depolarized cells have been known as far back as the 19th century. Generally, an air depolarized cell draws oxygen from air of the ambient environment, for use as the cathode active material. Because the cathode active material need not be carried in the cell, the space in the cell that would have otherwise been required for carrying cathode active material can, in general, be utilized for containing anode active material.
- 15 [0003] Accordingly, the amount of anode active material which can be contained in an air depolarized cell is generally significantly greater than the amount of anode active material which can be contained in a 2-electrode cell of the same overall size. By "2-electrode" cell, we mean an electrochemical cell wherein the entire charge of both anode active material and cathode active material are contained inside the cell structure when the cell is received by the consumer.
- 20 [0004] Generally, for a given cell size, and similar mass, an air depolarized cell can provide a significantly greater number of watt-hours of electromotive force than can a similarly sized, and similar mass, 2-electrode cell using the same, or a similar, material as the anode electroactive material.
- [0005] Several attempts have been made to develop and market commercial applications of metal-air cells. However, until about the 1970's, such cells were prone to leakage, and other types of failure.
- 25 [0006] In the 1970's, metal-air button cells were successfully introduced for use in hearing aids, as replacement for 2-electrode cells. The cells so introduced were generally reliable, and the incidence of leakage had generally been controlled sufficient to make such cells commercially acceptable.
- [0007] By the mid 1980's, zinc-air cells became the standard for hearing aid use. Since that time, significant effort has been made toward improving metal-air hearing aid cells. Such effort has been directed toward a number of issues. For example, efforts have been directed toward increasing electrochemical capacity of the cell, toward consistency of performance from cell to cell, toward control of electrolyte leakage, toward providing higher voltages desired for newer hearing aid appliance technology, toward higher limiting current, and toward controlling movement of moisture into and out of the cell, and the like.
- 30 [0008] An important factor in button cell performance is the ability to consistently control movement of the central portion of the cathode assembly away from the bottom wall of the cathode can during final cell assembly. Such movement of the central portion of the cathode assembly is commonly known as "doming."
- 35 [0009] Another important factor in button cell performance is the electrical contact between the cathode current collector and the cathode can or cathode terminal. Conventional cathode current collectors comprise woven wire screen structure wherein ends of such wires provide the electrical contact between the cathode current collector and the inner surface of the cathode can.
- 40 [0010] While metal-air button cells have found wide-spread use in hearing appliances, and some use as back-up batteries in computers, air depolarized cells have, historically, not had wide-spread commercial application for other end uses, or in other than small button cell sizes.
- [0011] The air depolarized button cells readily available as items of commerce for use in hearing aid appliances are generally limited to sizes of no more than 0.6 cm<sup>3</sup> overall volume. In view of the superior ratio of "watt-hour capacity/mass" of air depolarized cells, it would be desirable to provide air depolarized electrochemical cells for other applications. It would especially be desirable to provide air depolarized electrochemical cells which are relatively much larger than button cells. For example, it would be desirable to provide such cells in "AA" size as well as in the standard button cell sizes.

## 50 SUMMARY OF THE INVENTION

- [0012] The present invention in its various aspects is as claimed in the independent claims with optional features recited in the dependant claims.
- [0013] Embodiments of the invention can provide:

- 55 an air depolarized button cell having structure enabling improved control of doming;  
 an air depolarized cell having improved electrical contact between the cathode current collector and the cathode terminal r cathode can;

5 [0030] The invention further comprehends a method of fabricating a tubular air cathode assembly for use along an elongate side wall of an elongate air depolarized electrochemical cell. The method comprises fabricating an elongate tubular cathode current collector having an elongate side wall defining a tubular cross-section and an array of perforations extending through the side wall; mounting the elongate tubular cathode current collector on a mandrel having a cross-section, defining an arc having a radius smaller than an arc defined by the tubular cross-section of the cathode current collector; fabricating a carbon sheet comprising catalytically active carbon, and up to about 10 percent by weight of a binder; passing a such carbon sheet through a nip defined between (i) the combination of the mandrel and the cathode current collector and (ii) a support structure having greater arc radius than the arc radius of the mandrel; and applying force at the nip sufficient to apply and consolidate the carbon sheet onto an outer surface of the side wall of the cathode current collector.

10 [0031] Preferred methods include applying sufficient force at the nip to deform portions of the carbon sheet into the perforations, thereby mechanically securing the carbon sheet to the cathode current collector.

[0032] The method can include employing a support structure having greater arc radius than the arc radius of the mandrel by a ratio of at least 4/1, preferably at least 8/1, still more preferably at least 16/1, including a support structure having substantially an infinite arc radius, or a support structure having an inverse, concave curvature.

15 [0033] In preferred embodiments, the invention contemplates, after consolidating the carbon sheet onto the cathode current collector, and while retaining the assemblage of the cathode current collector and the carbon sheet on the mandrel, passing air diffusion material into and through the nip, and applying force at the nip sufficient to apply and consolidate the air diffusion material onto the carbon sheet, preferably using at least two, more preferably at least 3, endless layers of air diffusion material thereby to fabricate onto the carbon sheet a unitary, multiple layer, air diffusion member.

[0034] The method can further comprise aligning the air diffusion material so as to extend outwardly beyond the edge of the cathode current collector, and folding the outwardly extending portion inwardly about the edge of the cathode current collector and against an inner surface of the cathode current collector.

25 [0035] The method preferably includes applying liquidous seal rings on the air diffusion member adjacent opposing ends of the cathode current collector.

[0036] The invention still further contemplates a method of fabricating a tubular air cathode assembly for use along an elongate side wall of an elongate air depolarized electrochemical cell. The method comprises fabricating an elongate tubular cathode current collector having an elongate side wall defining a tubular cross-section, and an array of perforations extending through the side wall; mounting the elongate tubular cathode current collector on a mandrel having a cross-section, defining an arc having a radius smaller than an arc defined by the tubular cross-section of the cathode current collector, and mounting the combination of the mandrel and the cathode current collector in a stack of assembly rolls; fabricating carbon sheet structure comprising catalytically active carbon, and up to about 10 percent by weight of a binder, and thereby forming sheet structure of the catalytically active carbon composition, having a machine direction and a cross direction; making a sheet stack of respective overlying underlying ones of at least first and second elements of the carbon sheet structure, such that the sheet stack has a top and a bottom, and a thickness therebetween; passing the sheet stack through a nip and thereby applying force to the stack such that the applied force effects reduction in the thickness of the stack, in combination with consolidation of the respective elements of the carbon sheet structure into a unitary composite carbon sheet; and passing the so-consolidated carbon sheet into the stack of assembly rolls and thus through a plurality of nips acting between the mandrel/current collector and respective ones of the assembly rolls, and applying force at the nips sufficient to collectively apply and consolidate the consolidated carbon sheet onto an outer surface of the elongate side wall of the cathode current collector.

40 [0037] The method preferably includes collectively applying sufficient force at the nips to deform portions of the carbon sheet into the perforations, thereby mechanically securing the carbon sheet to the cathode current collector and, after consolidating the carbon sheet onto the cathode current collector, and while retaining the assemblage of the cathode current collector and the carbon sheet on the mandrel, passing an air diffusion material into the stack of assembly rolls and thus through the plurality of nips, and applying force at the nips collectively sufficient to apply and consolidate the diffusion material onto the carbon sheet.

45 [0038] The invention can include stretching the air diffusion material while passing it into the stack of assembly rolls and thus through the plurality of nips, and applying a sufficient length of such stretched air diffusion material to the carbon sheet to wrap the carbon sheet in at least two, preferably at least three, endless layers of stretched air diffusion material, thereby to fabricate onto the carbon sheet a unitary, stretched multiple layer air diffusion member.

50 [0039] As in the previous embodiment, this embodiment contemplates aligning the air diffusion material so as to extend outwardly beyond an edge of the cathode current collector, and folding the outwardly extending portion inwardly about the edge of the cathode current collector and against an inner surface of the cathode current collector, and optionally, applying liquidous seal rings on the air diffusion member adjacent opposing ends of the cathode current collector.

55 [0040] The invention further comprehends an air depolarized electrochemical cell comprising an anode, a cathode,

[0071] FIGURES 26-27 are representative cross-sections of bottom portions of cathode cans made using pre-forms of FIGURE 25.

[0072] FIGURE 28 is a representative cross-section showing a wide seal bead being formed at the bottom flange of the cathode can.

5 [0073] FIGURE 29 is a photograph showing a cross-section of the bottom portion of a partially assembled cell, configured as the bottom portion of the cell in FIGURE 26, and made using in situ melting as the method of placing the bottom seal.

[0074] FIGURE 30 is a representative cross-section of a cell of the invention similar to the cell of FIGURE 2, and illustrating an alternate top seal structure.

10 [0075] FIGURE 31A is a representation of a photograph showing a cross-section of a portion of a cell which has undergone significant discharge, wherein the zinc was loaded into the anode cavity in generally dry condition, and illustrating progression of the reaction front from the cathode current collector toward the anode current collector.

[0076] FIGURE 31B is a representation of a photograph showing a cross-section of a portion of a cell which has undergone significant discharge, wherein the zinc was loaded into the anode in a wet or gelled condition, and illustrating

15 progression of the reaction front from the cathode current collector toward the anode current collector.  
[0077] FIGURE 32 is a cross-section of a cell of the invention as in FIGURE 2, and employing a hollow tubular anode current collector as a mass-control chamber.

[0078] FIGURE 33 is a cross-section of a can-less embodiment of a cell of the invention.

[0079] FIGURE 34 is a fragmentary cross-section showing top and bottom portions of the cell of FIGURE 33, further enlarged.

20 [0080] FIGURES 34A-34D illustrate cross-sections of additional embodiments of top closure structure of the cell.

[0081] FIGURES 35 and 36 show representative elevation views of apparatus useful for closing and crimping the top and bottom members of can-less embodiments of cells of the invention.

[0082] FIGURE 37 shows a cross-section of a can-less embodiment of cells of the invention, utilizing a hollow anode current collector.

25 [0083] FIGURE 38 shows a cross-section of a can-less embodiment of cells of the invention, utilizing a hollow anode current collector, having central openings in both the top and the bottom of the cell.

[0084] FIGURE 39 illustrates a cross-section as in FIGURE 38, and utilizing a modified bottom structure of the cell.

[0085] FIGURE 39A is a fragmentary cross-section showing top and bottom portions of the cell of FIGURE 39, further enlarged.

30 [0086] The invention is not limited in its application to the details of construction or the arrangement of the components set forth in the following description or illustrated in the drawings. The invention is capable of other embodiments or of being practiced or carried out in various ways. Also, it is to be understood that the terminology and phraseology employed herein is for purpose of description and illustration and should not be regarded as limiting. Like reference numerals are used to indicate like components.

## DESCRIPTION OF THE ILLUSTRATED EMBODIMENTS

40 [0087] An elongate cylindrical metal-air cell 10 is shown in pictorial view in FIGURE 1. A longitudinal cross-section of the cell of FIGURE 1 is shown in FIGURE 2. An enlarged portion of the cross-section of the cell of FIGURE 2, at the bottom of the cell, is shown in FIGURE 3A. An enlarged portion of the cross-section of the cell of FIGURE 2, at the top of the cell, is shown in FIGURE 3B.

45 [0088] The structure of cell 10 represents the result of applicant drawing on a combination of technologies including from, among other places, (i) 2-electrode cylindrical bobbin cell technology (e.g. zinc-manganese dioxide round cells), and (ii) zinc-air hearing aid cell technology (zinc-air button cells), and making novel combinations using such information, in addition to elements novel in and of themselves, in arriving at cell 10 as illustrated, as well as other embodiments of the invention.

[0089] As with zinc-air button cells, the active air cathode assembly in an elongate cell of the invention is quite thin, allowing for a large fraction of the cell volume to potentially be occupied by zinc anode material, thus providing for disposition of anode material in close proximity with the air cathode assembly adjacent the outer cylindrical sides of the elongate cell, as well as allowing for increased weight of anode material in the elongate cell. Greater anode weight potentially enables the cell to deliver about two to three times the discharge watt-hours of a standard 2-electrode alkaline zinc-manganese dioxide cell of the same size and configuration.

55 [0090] The dominant electrochemical reactions associated with operation of zinc-air cells, in general, are generally considered to be as follows.

ports electric current at and through, to and from, the cathode. The cathode current collector generally provides that structural material which contributes most to defining the overall length, and the inner diameter, of the air cathode. In the embodiment illustrated in FIGURE 4, the current collector further provides substantially all the structural hoop strength present in the air cathode.

5 [0100] A preferred embodiment of cathode current collector 32 for use in an elongate cylindrical cell is illustrated in FIGURE 4 and is generally made from a square or otherwise rectangular, perforated metal sheet 40, illustrated in FIGURE 5. Metal sheet 40 has top and bottom edge portions 42, 44, respectively, and right and left edge portions 46, 48, respectively. As illustrated in FIGURES 4 and 5, top and bottom edge portions 42, 44, and right and left edge portions 46, 48, are preferably not perforated like the remainder of sheet 40.

10 [0101] While top and bottom edge portions 42, 44, and right and left edge portions 46, 48, can have some perforations in some embodiments, the high level of perforations extant over the remaining majority of sheet 40 is not preferred in especially right and left edge portions 46, 48.

[0102] For a "AA" size elongate cell, top and bottom edge portions 42, 44 typically have widths "W1" of about 0.1 inch. See FIGURE 6. As discussed hereinafter, bottom edge portion 44 provides a smooth surface for facilitating electrical contact between current collector 32 and the cathode can. Top edge portion 42 provides a smooth surface for assisting in creating a seal against leakage of liquid electrolyte past the cathode assembly and grommet 18.

15 [0103] Current collector 32 can be fabricated from a metal sheet as illustrated in FIGURE 5 into a cylindrical configuration such as that shown in FIGURE 4 by, for example, welding, such as laser butt welding (FIGURES 4A, 4B), respective left and right distal edges 50, 52 of edge portions 46, 48 to each other to create a joint 54 along the length of the cylindrically configured sheet 40, thereby to fixedly secure the cylindrical configuration.

20 [0104] While joint 54 can be formed by e.g. welding overlapped elements of the structure of edge portions 46, 48, the resulting double thickness of sheet material 40 at the resulting joint 54 is not preferred. Accordingly, joint 54 is preferably fabricated without layer-on-layer overlapping of the structures of edge portions 46, 48 one on the other. Rather, distal edges 50, 52 are preferably butted against each other in fabrication of the butt welded embodiments shown in e.g. FIGURES 4A, 4B.

25 [0105] The illustrated e.g. butt welding thus creates longitudinal joint 54, which can be a series of spot welds (FIGURE 4B), or can be a continuous weld (FIGURE 4A). Any other operable method of joining edges 50, 52 which thereby effectively converts metal sheet 40 into the cylindrical, or otherwise closed, configuration seen in FIGURE 4, is acceptable. The recited exemplary and preferred laser butt welding of metal sheet 40 can be done by Laser Services, Inc., Westford, Massachusetts, USA.

30 [0106] Right and left edge portions 46, 48 typically have widths "W2" of about 0.03 inch, to provide desirable quantities of material from which butt weld 54 can be formed.

[0107] Metal sheet 40 includes perforations 56 (FIGURES 5, 6, 7) extending through the thickness "T1" (FIGURE 7) of metal sheet 40, from outer surface 58 to inner surface 60. A typical such metal sheet, suitable for fabricating cylindrical current collector 32 for a "AA" size elongate cell, contains about 4000 of such perforations 56 as illustrated by Table 1. The number of perforations depends on the sizes and configurations of the perforations, and the widths "W3" of webs 62 between the respective perforations. Perforations 56 are preferably regular hexagons, measuring about .02 inch between opposing straight sides thereof. In the embodiments illustrated in FIGURES 4, 5, and 6, the widths "W3" of webs 62 are preferably also about 0.02 inch. Accordingly, in the embodiments illustrated in FIGURES 4, 5, and 6, perforations 56 represent about 65% of the overall surface area of metal sheet 40. In general, for a cell intended for use to deliver a high rate of electrical discharge, perforations 56 should usually represent about 45% to about 70% of the overall surface area of that portion of metal sheet 40 which is perforated.

35 [0108] While perforations 56 have been illustrated as regular hexagons, a variety of other shapes are acceptable. There can be mentioned, for example, circles, squares, and e.g. equilateral triangles. Circular perforations 56 are illustrated in current collector 32 shown in FIGURE 8. Square perforations 56 are illustrated in current collector 32 shown in FIGURE 9. However, because of advantageous resulting strength of the so-fabricated cathode current collector, and effective securement of the active cathode catalyst to current collectors having hexagonal perforation, regular hexagonal perforations 56, as illustrated in FIGURES 5 and 6, are preferred. After hexagons, the other shapes which create corners are preferred because the corners improve securement of the active cathode catalyst to the current collector, as compared to, for example, circles, ellipses, and like shapes which are devoid of corner structure where two side edges of the corresponding opening come together.

40 [0109] Table 1 illustrates typical parameters of various perforations such as those shown in FIGURES 5 and 6 for a cathode current collector sized for a "AA" size elongate cell. The column labeled "Open %" refers to that portion of the metal sheet which is perforated, irrespective of edge portions 42, 44, 46, 48.

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[0117] Accordingly, the actual number of perforations used in a particular implementation of the invention results from balancing the benefit, if any, in the particular use for which the cells are planned, of a larger number of smaller perforations against the cost of making such larger number of smaller perforations.

[0118] The acceptable range of the number and sizes of perforations, of course, depends on the size of the overall surface area of metal sheet 40 being perforated. Thus, where a larger cell is being fabricated, and a respectively larger overall surface area of metal sheet is being perforated as the current collector, the upper end of the range of the acceptable number of perforations is increased accordingly. Where a smaller cell is being fabricated, and a respectively smaller overall area is being perforated as the current collector, the lower end of the range of the acceptable number of perforations is reduced accordingly.

[0119] In the preferred embodiment, perforations 56 as in FIGURES 5 and 6 are preferably fabricated by placing a suitable photo mask on metal sheet 40. The unmasked areas of the sheet are then acid etched to thereby fabricate the perforations.

[0120] In an alternate construction, current collector 32 can be made of woven wires rather than a perforated metal sheet. Preferred screen size corresponds to greater size wire and openings than 200 standard mesh size. Mesh sizes of about 16 to about 100 tend to work well. Mesh sizes 24, 37, and 40 work particularly well. Similar sizes for perforations 56 and webs 62 are contemplated in the embodiments made with etched metal sheet.

[0121] In some embodiments, metal sheet 40 is perforated right up to and including right and left distal edges 50, 52, while edge portions 42, 44 are retained imperforate, whereby edge portions 46, 48 are obviated. Further, woven wire embodiments may not include imperforate edge portions 46, 48. In such embodiments, butt welding of distal edges 50, 52 to create joint 54 is somewhat more difficult because of the void spaces between webs 62 at distal edges 50, 52, or between adjacent wires in woven wire embodiments. In place of butt welding, cooperating webs 62, or corresponding wires 62, can be interdigitated, and edges of such interdigitated webs or wires can be welded together as a third example of methods of forming joint 54. Given the greater precision required for joiner of edges 50, 52, where perforations 56 extend to edges 50, 52, fabrication considerations suggest that such embodiments are not preferred:

[0122] In still other embodiments, metal sheet is perforated right up to top and bottom distal edges 57, 59, while edge portions 46, 48 are or are not retained imperforate, whereby edge portions 42, 44 are obviated. In such embodiments, use of the upper edge area of cathode current collector 32 in forming a seal against electrolyte leakage may be somewhat degraded such that there may be a need to employ other provisions for leakage control. Similarly, use of the lower edge area of the cathode current collector as a contact surface for making electrical contact with the cathode can may be somewhat less robust than imperforate embodiments, such that other provisions for electrical contact may be employed. However, such spaced contacts between the cathode current collector and the cathode can or other cathode terminal is routinely used with satisfactory result, in air depolarized button cells. Nonetheless, considerations of performance potential suggest that perforations up to top and bottom distal edges 57, 59 are not preferred.

[0123] Metal sheet 40 can be made from any material which provides suitable conductivity for collecting and transmitting the electrical current flowing through the cathode, while tolerating the alkaline electrolyte environment. Typical material for metal sheet 40 for embodiments illustrated in FIGURES 1, 2, 3A, 3B, 4, 5, 6, and 7, for a size "AA" elongate cell, is nickel sheet .005 inch thick. The range of thicknesses of the cathode current collector for a size "AA" cell is from about .003 inch to about .010 inch. Thinner materials outside the recited range may be difficult to fabricate, and may lack sufficient structural strength. Thicker materials may be too rigid to fabricate into annular shape. In addition, such thicker materials do use greater amounts of raw materials, and do occupy a greater fraction of the limited space available inside the cell.

[0124] The full complement of sizes within the recited range can be utilized in the invention, for example and without limitation, .004 inch, .006 inch, .007 inch, or .008 inch. Thinner material is preferred where emphasis is placed on minimizing the thickness of non-reactive materials, thus to provide greater internal volume inside the cell for packing in a greater quantity of electroactive anode material or thus to control weight of the cell. Thicker material is preferred where emphasis is placed on physical strength and/or rigidity of the air cathode assembly.

[0125] Hoop strength of annular current collector 32 as in FIGURE 4 is related to the mathematical square of the thickness of sheet metal 40. Thus, the strength of a current collector .007 inch thick has approximately two times the hoop strength ( $7 \times 7 = 49$ ) of a corresponding current collector which is .005 inch thick ( $5 \times 5 = 25$ ). Overall, the ratio of the strength of the .007 inch thick current collector to the strength of the .005 inch thick current collector is thus  $49/25 = 1.96/1$ .

[0126] In other embodiments, metal sheet 40 is replaced with e.g. cross-bonded woven wire of a size similar to metal sheet 40. In such structure, the wires generally take the place of webs 62. The diameter of such woven wire is generally about .003 inch to about .010 inch thick and includes the full complement of sizes within the recited range, as recited herein for the sheet metal thickness. Current collectors can be fabricated from such wire by butt welding, as in FIGURE 4, adjoining surfaces of respective cooperating wires in the weave. In place of butt welding, cooperating wires can be interdigitated as discussed herein above, and cooperating edges of such interdigitated wires welded together, as shown in FIGURE 4C. The bottom edge of FIGURE 4C illustrates perforations 56 extending to the distal edge 59 of the bottom

and the same structures, as are recited above for current collector 32. Any known method for making perforations in metal sheet can be used to make perforations 56A, including the use of woven wire to fabricate the perforated central region, or the above noted combination of photo mask and acid etching of metal sheet. Thus, "perforated," "imperforate," and like expressions include, without limitation, both perforated metal sheet material, woven wire articles, and articles made of woven web material. Web material is an elongate wire-like or strap-like structure having width greater than top-to-bottom thickness.

[0138] Perforations 56A, and the corresponding webs, can have any of the shapes and configurations described above for perforations 56 such as square, circular, hexagonal, and the like.

[0139] FIGURE 5C illustrates generally a process for fabricating current collectors 32A. As suggested in FIGURE 5C, cooperating registration holes 533 are fabricated along opposing edges 535, 537 of a suitable metal strip 539 having thickness and composition consistent with the above recited thicknesses and compositions. Suitable photo mask and acid etching are then employed, in cooperation with registration holes 533, thereby to fabricate multiple spaced circular arrays 541 of perforations 56A representing respective central portions 55A of precursors of current collectors 32A. The respective arrays 541 are subsequently punched from metal strip 539, along with a corresponding border region about each array, to thus fabricate a corresponding number of cathode current collectors 32A. As an array is punched out of strip 539, the correspondingly punched border region becomes region 61A in the respective current collector 32A.

[0140] An advantage of the border region 61A, as compared to a current collector made entirely of woven wire or the like, is that the entire outer edge 67A of the border region is available for making electrical contact with the cathode can whereas only ends of the respective wires are so available in a current collector made entirely from wire, for making electrical contact with the cathode can. In addition, the border region participates in the formation of an effective seal against leakage of electrolyte out past the grommet and thence out of the cell.

#### THE ACTIVE CARBON CATALYST

[0141] Active carbon catalyst 34 is generally supported on current collector 32. The active carbon catalyst provides reaction sites where oxygen from the air reacts with water from the electrolyte, e.g. according to the above cathode half reaction, to generate the hydroxyl ions which are later used in the anode to release electrons, e.g. according to the anode half reaction. Carbon particles in the active carbon catalyst thus provide solid reaction sites for the air/liquid interface where aqueous liquid and gaseous oxygen come together and effect the electroactive cathode half reaction.

[0142] The carbon catalyst cooperates with the current collector in collecting and/or conducting current within the cathode in support of the cathode half reaction.

[0143] In order to limit internal resistance in the cathode, during the process of joining carbon catalyst to the current collector, the carbon catalyst is brought into intimate contact with current collector 32, including and especially at perforations 56. Referring to FIGURES 3A, 7 and 10, carbon catalyst 34 preferably extends through perforations 56 and extends outwardly of the projections of perforations 56 at and adjacent inner surface 60 of current collector 32. Thus, the carbon catalyst is generally intimately interlocked with current collector 32, through perforations 56, about the perimeter edges of the respective perforations, at both outer and inner surfaces 58, 60 of the current collector.

[0144] Referring to FIGURE 10, upon completion of assembly of the carbon catalyst to the cathode current collector, carbon catalyst 34 preferably covers the entirety of that portion of cylindrical outer surface 58 of the current collector which lies between top edge portion 42 and bottom edge portion 44.

[0145] Carbon catalyst 34 is a combination of carbon particles, a binder, and processed potassium permanganate. During processing of the potassium permanganate in creating carbon catalyst 34, the carbon reduces the manganese to valence state +2 (hereinafter "manganese (II)"). The combination of valence state +2 manganese, with suitably activated carbon, acts successfully as catalyst for reduction of oxygen in air cathodes. As a result of in situ reactions, catalytically active manganese (II) forms in the matrix of the active carbon catalyst.

[0146] Carbon catalyst 34 can be fabricated, and mounted on current collector 32 as follows. The carbon used in fabricating catalyst 34 is represented by carbon particles having surface area greater than 50 square meters per gram ( $\text{m}^2/\text{g}$ ), preferably greater than  $150 \text{ m}^2/\text{g}$ , more preferably greater than  $250 \text{ m}^2/\text{g}$ , still more preferably between about  $250 \text{ m}^2/\text{g}$  and  $1500 \text{ m}^2/\text{g}$ , yet more preferably between about  $700 \text{ m}^2/\text{g}$  and  $1400 \text{ m}^2/\text{g}$ , further more preferably between about  $900 \text{ m}^2/\text{g}$  and  $1300 \text{ m}^2/\text{g}$ , and most preferably between about  $1000 \text{ m}^2/\text{g}$  and  $1150 \text{ m}^2/\text{g}$ .

[0147] In a preferred embodiment, carbon of the present invention has the following characteristics; surface area between  $1000 \text{ m}^2/\text{g}$  and  $1150 \text{ m}^2/\text{g}$ , apparent density of about  $0.47 \text{ g/cc}$  to about  $0.55 \text{ g/cc}$ , preferably about  $0.51 \text{ g/cc}$ ; real density of about  $1.7 \text{ g/cc}$  to about  $2.5 \text{ g/cc}$ , preferably about  $2.1 \text{ g/cc}$ ; pore volume of about  $0.80$  to about  $1.0 \text{ cc}$ ; specific heat at  $100^\circ \text{C}$  of about  $0.20$  to about  $0.30$ , preferably about  $0.25$ ; and about  $65\%$  to  $75\%$  of such material will pass through a wet  $-325$  US Standard mesh screen wherein the nominal opening size is  $.0017$  inch ( $.045 \text{ mm}$ ). Such preferred carbon is available as PWA activated carbon from Activated Carbon Division of Calgon Corporation, Pittsburgh, PA.

minutes, or until any and all agglomerates in the mixture are broken down, and the mixture becomes free flowing, thereby to make a free-flowing powder mixture 64.

[0157] The resulting free flowing powder mixture 64 is rolled into web form in a manner generally illustrated in FIGURE 11. Referring to FIGURE 11, carbon powder mixture 64 is placed in a hopper 66 and fed downwardly through the hopper to a discharge opening such as slot 68, which feeds the powder mixture to a first nip formed by a pair of polished steel rolls 70 at suitable speed to position a sufficient amount of the carbon powder mixture above the nip formed between the rolls, with which to form a generally continuous web of such powder mixture. Rolls 70 are driven in cooperating directions illustrated by arrows 72, at constant common speeds, thus to draw the powder into the nip between the rolls. The spacing between rolls 70 is set at a fixed distance sufficient to draw the carbon powder mixture into the nip and, by the pressure exerted on the carbon powder mixture as the mixture passes through the nip, to fabricate the carbon powder mixture into a web 74, having a thickness of about 0.004 to about 0.010 inch, preferably about .004 inch to about .006 inch, and a with machine direction (MD) and a cross machine direction (CD). The constant speed of rolls 70 produces a web 74 having a relatively uniform thickness along the length of the web.

[0158] While the web fabricated at rolls 70 can thus be consolidated from powder form to a single web body, the web so fabricated is quite fragile.

[0159] After the web is consolidated as illustrated in FIGURE 11, the web may be wound up as a roll (not shown) or otherwise consolidated or packaged for storage and/or shipment. In some embodiments, web 74 is cut cross-wise (along the CD direction) to thereby produce individual, e.g. generally rectangular sheets 80, illustrated in FIGURE 12. In such embodiments, 2 to about 6 such individual sheets 80 are stacked on top of each other with the machine direction (MD) in sequential sheets in the stack being oriented transverse, preferably perpendicular, to each other. FIGURE 12A shows such a stack 82 of 4 sheets 80A, 80B, 80C, 80D. Arrows 84 indicate the MD in each sheet, illustrating the sheets being oriented perpendicular to each other. A stack of 4 such sheets, each having a thickness of about 0.005 inch, has a combined thickness of nominally about .020 inch.

[0160] With sheets 80 so stacked and arranged, the 4-sheet stack is passed through a second nip illustrated by rolls 86. Rolls 86 are shown spaced apart for illustration purposes in FIGURE 12A. The spacing at the nip between rolls 86 is set and held at a uniform nip gap significantly smaller than the sum of the thicknesses of the sheets in the stack.

[0161] The size of the spacing between rolls 86 at the gap should be less than 75% of the combined thicknesses of the sheets making up the stack. Preferred size of the spacing is from about 20% up to about 60% of the combined free thicknesses of the sheets making up the stack, with a more preferred range of about 25% to about 40% of the combined thicknesses.

[0162] During processing of the stack 82 of sheets, rolls 86 preferably rotate at a generally constant speed in cooperating directions illustrated by arrows 87, and thereby draw the stack into the nip, thus working the composite 4-sheet stack. As stack 82 passes through the nip, the sheets are, in combination, mechanically worked by rolls 86, with the result that the worked composite sheet stack 82W is significantly stronger than the unworked sheets, whether taken alone or in combination. The composite sheet stack is preferably so worked in suitable nips, preferably from 2 to about 6 times, or more, until the worked composite sheet stack is suitably toughened or otherwise strengthened that the resulting worked composite sheet stack 82W can be handled by commercial speed production equipment in fabricating elongate electrochemical cells of the invention having cathode assemblies having generally arcuate configurations generally corresponding with the outer arcuate sides of the respective cells.

[0163] The overall effect of the working of the stack of sheets is to reduce the thickness of the stack and to effectively cross-bond and thereby consolidate the sheets to each other, such that the directionality of the strength of web 74 (e.g. the MD/CD ratio of tensile strength) is more evenly distributed in the MD and CD directions in the thus-consolidated, unitary worked sheet 82W than in an unworked sheet of similar thickness. Namely, the ratio of crossing tensile strengths is closer to "1" in the unitary worked sheet than in the unworked sheets, whether the unworked sheets are taken individually or in combination. In addition, applicants contemplate that the work done in the first and second nips at rolls 70 and 86 further fibrillates the binder, and interconnects the associated fibrils, into a three-dimensional net-like arrangement of interconnected binder fibrils, thus to assist the binder in its role of binding the carbon and Mn(II) moieties into the resulting worked sheets 82W, or otherwise containing or holding the carbon and Mn(II) moieties in sheet form. As a mechanical act, the contemplated three-dimensional net-like binder arrangement is believed to receive and hold the carbon particles in the sheet structure, primarily by mechanical entrapment.

[0164] PTFE, as a binder, can also serve as a chemical bonding agent, bonding carbon particles together to form an adhesively-defined matrix. While adhesive properties of PTFE are generally activated by heat, applicants contemplate that the work energy utilized in the working of the stack of carbon sheets as at the nip formed by rolls 70 and 86 may be effective to so heat the compositions of the materials being rolled as to concomitantly and concurrently activate the adhesive properties of the PTFE. Applicants thus contemplate that the binding performance of the PTFE in active carbon catalyst of the invention may be a combination of mechanical entrapment and such chemical adhesion.

[0165] The resulting worked sheet 82W is sufficiently strong, in all directions, to tolerate commercial processing. The typical worked sheet has an overall thickness in the range of about .003 to about .010 inch, preferably about .004 to



of the cathode current collector, and defines substantially the entirety of the inner surface of the combination of the current collector and the carbon material.

[0176] The common and relatively constant speeds of rolls 92 provide a generally uniform thickness "T2" to the resulting layer of carbon-based material which is applied to the outside surface 58 of cathode current collector 32.

[0177] In the embodiment illustrated in FIGURE 14, the pressure on the carbon sheet workpiece and on the cathode current collector in stack 90 is applied by a pair of pneumatic cylinders (not shown) having working diameters (cylinder bore size) of 1.06 inches. The pneumatic cylinders urge top roll 92A downwardly against the outer surface of current collector 32 as illustrated by arrows 95, and apply force through current collector 32 and mandrel 93 against bottom rolls 92B, 92C.

[0178] As illustrated in FIGURE 14, downward force on top roll 92A is transferred through current collector 32 to mandrel 93 at top roll 92A, and from mandrel 93 back through current collector 32 to rolls 92B, 92C at the interfaces of rolls 92B, 92C with current collector 32. Accordingly, when downward force is applied to roll 92A, with mandrel 93 and current collector 32 in place as seen in FIGURE 14, the force passes through mandrel 93 and is applied to current collector 32, substantially simultaneously, at the 3 locations of linear contact, namely the three nips, between current collector 32 and respective rolls 92A, 92B, 92C.

[0179] The relationship of the mandrel in the stack is such that the mandrel is held in the stack generally by the forces applied by the stack of rolls. Namely, the mandrel generally floats, in surface-to-surface contact with rolls 92A, 92B, 92C, within the opening defined between rolls 92A, 92B, 92C, both when rolls 92A, 92B, 92C are motionless, and when the rolls are turning in performance of the operations the rolls were designed to accomplish.

[0180] As work piece 88 is introduced into the nip, the force being applied by the top roll against the current collector is thus imposed on the work piece, and much of the respective force is accordingly transmitted through the work piece to the current collector. As the work piece is drawn into the stack of rolls, force is first applied to the leading edge of the work piece by roll 92A.

[0181] As the work piece leading edge progresses past roll 92A, the movement of the leading edge out of the nip at roll 92A correspondingly releases the nip force from the leading edge, and such force is correspondingly applied and released twice more as the leading edge respectively passes through the nips defined between rolls 92B and 92C and current collector 32. The remaining portions of the carbon sheet work piece are likewise subjected to three consecutive applications of lines of force at rolls 92A, 92B, 92C, with corresponding releases of the force between respective force applications as such portions pass into and through the respective working nips. Thus, when the full length of the work piece has been received into the stack of rolls, and the stack is effecting rotation of the work piece in the stack, force is being simultaneously applied to the work piece at three spaced lines extending along the length of current collector 32 and respectively along the width of work piece 88. It will be understood that force is being applied constantly and uniformly to the rolls, and that the application and release of force to current collector 32 and work piece 88 is a result of the current collector and work piece passing between a roll and the current collector (force applied) and out from between a roll and the current collector (force released), all while a preferably uniform force is being constantly applied to roll 92A, and thus at the three nips.

[0182] In the above process, some of the force at one or more of rolls 92A, 92B, 92C performs the above noted step of deforming the soft and pliable material of work piece 88, thereby to extrude the carbon material into perforations 56 as illustrated. The extent of the extrusion or other deformation of the workpiece at any given locus about the circumference of the outer surface of the current collector is a function of the nature and amount of forces applied at that locus by rolls 92A, 92B, 92C at their respective lines of contact with the work piece, in combination with the time over which the respective forces are applied as well as being a function of the nature of the surfaces of rolls 92A, 92B, 92C. As force is increased for a given time interval over which the force is applied, in general, the amount of material deformed through perforations 56 increases.

[0183] The length of work piece 88 is defined herein to be long enough to assuredly cover the entire circumference of current collector 32. As noted above, the forces applied on the work piece as the work piece is being assembled to the current collector cause the work piece to deform. Such deformation includes deformation of the length and width dimensions, as well as the above described deformation of the thickness parameters. Accordingly, considering the plastic deformation of work piece 88, in order to ensure that the work piece fully covers the circumference of the current collector, the length of the work piece is specified such that the deformed length will be slightly longer than is expected to be needed to fully cover the circumference of the current collector. Thus, by the time the full length of the work piece has been received at roll 92A, and the work piece has been plastically deformed in length, width, and thickness by the forces applied by stack 90 of rolls, the trailing edge of the work piece slightly overlaps the leading edge of the work piece on the current collector.

[0184] As the trailing edge of the work piece is pressed onto the current collector, and progresses about stack 90, the forces of rolls 92A, 92B, 92C, physically and plastically deform the combination of the leading and trailing edges thus to create a smooth boundary between the leading and trailing edges of the work piece in application of the carbon-based material to the cathode current collector, to thus form, mount, bind, secure, and otherwise join the active carbon

192. One can also use an endless belt (not shown) presenting, under pressure, any desired curvature to cathode current collector 32, or to the carbon catalyst, at the respective nip, including a flat presentation e.g. an infinite radius (not shown), or an inverse concave curvature up to a curvature that more-or-less, or generally, follows the curvature of the cathode current collector as effected by mandrel 93. Thus, an arc radius ratio of at least about 4/1 includes flat presentations, and structures (e.g. inverted arcs) that tend to follow the outline of mandrel 93 and/or current collector 32. [0195] For use of the embodiment of FIGURE 14A to apply the carbon to the cathode current collector, the disclosed cylinders are preferably powered to about 40 psi to about 60 psi, more preferably about 50 psi.

#### AIR DIFFUSION MEMBER

[0196] Air diffusion member 36 preferably performs a variety of functions in the cell, and provides a variety of properties to the cell. First, diffusion member 36 provides a moisture barrier, tending to prevent, discourage, retard, or otherwise attenuate, passage of moisture vapor into or out of the cell.

[0197] Second, diffusion member 36 provides a liquid barrier, to prevent, retard, attenuate, or otherwise discourage leakage of liquidous electrolyte out of the cell.

[0198] Third, in preferred embodiments, diffusion member 36 provides a folded-over seal layer at the top of the cell. Such seal layer, in combination with the separator, physically and electrically isolates the cathode current collector and the active carbon catalyst from grommet 18 and anode mix 20.

[0199] Fourth, diffusion member 36 can be used to control the rate of diffusion of air into and out of the cell to and from the reaction sites on the active carbon catalyst. As such, the diffusion member sets the upper limit of the rate at which oxygen can reach the cathode reaction sites. To the extent the diffusion rate through the diffusion member is lower than the rate at which oxygen can be used at the reaction surface, namely the oxygen reaction rate, the diffusion member defines the upper limit of the cathode reaction rate at the reaction surface. By so controlling the cathode reaction rate, and assuming the anode reaction rate is not controlling, diffusion member 36 provides a control to the limiting current, namely that maximum current flow which can be produced by the cell when an external circuit which is powered by the cell operates under high demand conditions.

[0200] Fifth, diffusion member 36 distributes air laterally along its own length and width, especially the incoming air entering the cell. Such lateral distribution affects the degree to which oxygen is provided uniformly over the entirety of the area of the reaction surface of the cathode assembly, rather than having oxygen much more concentrated at those portions of the reaction surface which are directly opposite air ports 38 and correspondingly much less concentrated at those portions of the reaction surface which are between projections of the air ports onto the reaction surface.

[0201] In view of the above multiple functions of diffusion member 36, the material from which the diffusion member is fabricated must have certain properties. Such material must be sufficiently porous as to provide an adequate conduit for flow of oxygen therethrough, both through the thickness of the material and internally along the lateral length and width of the material. Suitable such materials are certain ones of the microporous polymeric films.

[0202] The material should be generally a barrier to transmission of water, whether in liquid or vapor form. Specifically, the air diffusion member serves as a barrier to loss of the liquid aqueous potassium hydroxide or similar electrolyte from the cell, through the air cathode and preferably attenuates movement of water vapor into or out of the cell. Since the electrolyte is an aqueous composition, the material from which the air diffusion member is fabricated must be generally hydrophobic. Certain ones of the microporous polymeric films are hydrophobic.

[0203] The material must be tolerant of, and generally inert to, the electrolyte, for example the alkaline electrolyte environment of aqueous potassium hydroxide-based electrolyte which is typical of metal-air electrochemical cells.

[0204] The material must embody suitable internal structure, and suitable surface properties, to provide sealing properties, for example, to provide, in combination with the separator, a pressure seal gasket-type effect at the top of the air cathode, thereby to provide a seal layer between the grommet and the cathode current collector. At the bottom of the cell, the material provides a seal between the bottom member of the cell and the combination of the cathode current collector and the active carbon catalyst.

[0205] The material from which air diffusion member 36 is fabricated is preferably subject to manipulation such as during fabrication in order to limit, namely to reduce to a desired amount, the rate at which oxygen and water vapor penetrate through the diffusion member and reach the reaction surface of active carbon catalyst 34. Such capacity for manipulating the air diffusion rate enables the cell manufacturer to control the target air diffusion specifications of the cells being manufactured by making changes in the assembly process without necessarily changing the raw material from which the air diffusion member is fabricated. To the extent the diffusion rate of water vapor can be so manipulated/reduced and controlled without limiting oxygen diffusion so much that the cathode reaction rate is reduced, passage of water vapor into or out of the cell can be correspondingly reduced without affecting the limiting current of the cell.

[0206] A preferred air diffusion member 36 for a "AA" size cell has a thickness of about .0035 inch. A suitable range of thicknesses is about 0.002 inch to about 0.006 inch, with a preferred range of about .0025 inch to about .005 inch, and a most preferred range of about 0.003 inch to about 0.004 inch. Such air diffusion member 36 can be fabricated

structure of the PTFE which defines the microporous nature of the PTFE strip forms mechanical affixations with the active carbon catalyst, thus mechanically "bonding" the PTFE to active carbon catalyst 34. Applicants contemplate that, at the same time, the stack pressure likely further deforms the carbon material into and through perforations 56.

[0219] As the rotating current collector, catalyst, and PTFE strip complete a full revolution in roll stack 90, the incoming PTFE begins to encounter, and to be fed over, the underlying first layer of the PTFE. The pressure being applied by roll stack 90 urges the overlying incoming PTFE material into intimate contact with the underlying PTFE material such that the microporous structure of the two layers of PTFE which defines the microporous nature of the PTFE strip forms mechanical affixations between the two PTFE layers, thus lightly mechanically "bonding" the overlying and underlying PTFE layers to each other. Third and subsequent layers of PTFE, if applied, mechanically bond to the respective underlying layers in a similar manner. In preferred embodiments, the PTFE strip is wrapped about 3.25 times around the outer circumference of the current collector-catalyst combination.

[0220] The result, of wrapping the PTFE strip about the current collector-catalyst combination multiple times without an intervening leading or trailing end edge of the strip, is the application of multiple layers of the PTFE without deploying multiple seams at layer joiners. Rather, the multiple layer diffusion member so fabricated is effectively seamless in that there is no intermediate seam, or series of seams defining the multiple layers, which seams could provide leakage paths for exodus of liquid electrolyte from cell 10. By providing a full number of wraps plus a modest overlap of the starting point on the circumference of the assembly, a full complement of the desired thickness is provided over the entire circumference of the assembly so created.

[0221] The terminal end edge of the strip is subjected to the same pressures as the rest of the strip. Accordingly, the same bonding principles bond the end edge of the strip to the underlying layer of PTFE, whereby the end edge of the strip is suitably bonded into the overall assembly. FIGURE 17 shows a representative cross-section of the cathode assembly assemblage at the instantly above-described stage of assembly, whereby about 3.25 circumferential wraps of the PTFE have been applied to the assemblage of the carbon on the cathode current collector.

[0222] In preferred embodiments, as the PTFE strip is fed into the nip formed between roll 92A and the active carbon catalyst, the strip is positioned such that a first side edge of the strip is aligned laterally with a first side edge of the current collector-catalyst combination, and the second edge of the strip extends, as an edge portion, outwardly of the opposing side edge of the current collector, which will be disposed toward the top of the cell, by preferably about 0.125 inch. Thus, when the PTFE strip has been fully assembled to the current collector-catalyst combination, thereby to apply the strip to the current collector-catalyst combination and to fabricate the diffusion member, one side edge of the multiple layers of PTFE strip extends outwardly of the corresponding top edge of the current collector.

[0223] As the PTFE strip is applied to and through the nip between roll 92A and carbon catalyst 34, pressure is applied by stack 90 directly to the PTFE strip, indirectly to workpiece 88, and indirectly to current collector 32, in the same manner as is used in assembling the active carbon catalyst to the current collector. Speed of rotation of the rolls is generally the same as described above for applying the active carbon catalyst material to the current collector. Pressure applied to the PTFE web by stack 90 is in the range of about 30 psi to about 100 psi, preferably about 35 psi to about 70 psi, still more preferably about 35 psi to about 50 psi.

[0224] Using the above described PTFE strip, and the above described pressure and speed on rolls 92A, 92B, 92C, the PTFE strip is compressed as it enters and traverses the stack, whereby the effective thickness of the sheet material is reduced as the strip is assembled with the current collector and the catalyst. Increased compressing of the PTFE in general reduces permeability of the PTFE to air flow therethrough. Permeability is also reduced as the number of layers of PTFE is increased.

[0225] Starting with a PTFE strip thickness of 0.002 inch, the overall thickness of a three layer diffusion member 36, so fabricated, is preferably about 0.0035 inch. This and other thicknesses of PTFE strip can accordingly be used, in this and other numbers of layers of PTFE strip material, for example, 4 layers, 5 layers, 6 layers, 7 layers, or more, to fabricate any desired thickness and/or any desired diffusion rate for diffusion member 36.

[0226] After the PTFE strip is thus assembled to the current collector-catalyst combination, the pressure is released from roll stack 90, and the current collector, carbon catalyst, diffusion member assemblage is removed from the stack.

[0227] A separator 16 is then juxtaposed adjacent the inner surface of the cathode assemblage. Separator 16 can be juxtaposed adjacent the inner surface either before or after the cathode assemblage is assembled to a bottom closure member such as to bottom closure member 202 or to cathode can 28.

[0228] The upstanding free edge region of the PTFE diffusion member is then rolled or folded inwardly about the circumference of the cell, down over the top of the separator, and downwardly onto the top portion of the inner surface of the separator. The downwardly-depending portion of the PTFE on the inner surface of the separator provides a seal shield, in slot 174 (FIGURE 3B), against movement of electrolyte or electricity from anode mix 20 through slot 174 and to the cathode current collector or the cathode can.

[0229] The rolling of the PTFE upstanding free edge region can, in theory, be done any time after the air cathode assembly is formed. The preferred sequencing is to roll the PTFE free edge shortly after removing the assembled air cathode from the stack of rolls 90.

such materials providing sufficient strength and ductility can also be used as single layer materials in place of the composite structure which comprehends CRS or other suitable material as a core layer.

[0244] Steel strip plated with nickel and nickel alloy is generally used because of cost considerations, and because pre-plated, or clad, steel strip, which generally require no post-plating processes, are commercially available. The metal in the can must be both ductile enough to withstand the drawing process, and strong and rigid enough, to tolerate and otherwise withstand the cell crimping and closure process as well as to provide primary overall structural strength to the cell during shipment of the cell to market, and during the contemplated use life of the cell.

[0245] Cathode cans, for example, can be made of cold-rolled steel plated with nickel. Cathode cans may also be formed from cold-rolled mild steel, with preferably at least the inside portions of the cans being subsequently post plated with nickel. Other examples of materials for cathode cans include nickel-clad stainless steel; nickel-plated stainless steel; INCONEL (a non-magnetic alloy of nickel); pure nickel with minor alloying elements (e.g. NICKEL 200 and related family of NICKEL 200 alloys such as NICKEL 201, etc.), all available from Huntington Alloys, a division of INCO, Huntington, West Virginia USA. Some noble metals may also find use as plating, cladding, or other coating for can metals, including covering steel strip plated with nickel, and mild steel strip subsequently plated with nickel after fabricating the can.

[0246] Where multiple layers are used, e.g. CRS coated on opposing sides with nickel, the invention contemplates additional e.g. fourth, fifth, etc. layers, either between the nickel and CRS, or with a nickel layer between the CRS and the additional layer(s). For example, gold, platinum, palladium, or other excellent electrical conductor can be deposited on some or all of the outer surface of the cathode can (outside the nickel layer) after the can is drawn, or drawn and ironed. As an alternative, such fourth etc. layer can be, for example, a bond-enhancing layer between the CRS and the nickel.

[0247] Where the can is fabricated using a typical raw material structure of /NI/CRS/NI/ as the sheet structure, such sheet structure is preferably about .010 inch thick, with a thickness range of about .006 inch to about .020 inch, and a preferred range of about .008 inch to about .014 inch. In such embodiments, each of the nickel layers represents about 2% to about 10%, preferably about 3% to about 7%, more preferably about 4% to about 6%, most preferably about 5%, of the overall thickness of the metal sheet in such 3-layer structure.

[0248] Cathode can 28 includes bottom wall 37, and side wall 39 extending upwardly from bottom wall 37. Given the above noted drawing, or drawing and ironing process used in making can 28, the thickness of bottom wall 37 is typically, but not necessarily, about 80% of the thickness of the raw sheet material from which the can was fabricated. Thus, where the raw sheet material from which the can was fabricated was .010 inch thick, the thickness of the bottom wall of a can made from such sheet material is typically about .008 inch.

[0249] Similarly, the thickness of side wall 39 is about 50% of the thickness of the raw sheet material from which the can was fabricated. Thus, where the raw sheet material from which the can was fabricated was .010 inch thick, the thickness of the side wall of a can made from such sheet material is typically about .005 inch.

#### CATHODE CAN SIDE WALL

[0250] After the basic shape and structure of the can are formed by drawing, or drawing and ironing, or other fabrication process, the finishing steps are performed on the side wall and the bottom wall. Accordingly, air ports 38 are formed in side wall 39. For the illustrated size "AA" cell, about 400 air ports 38 are preferably formed by e.g. laser piercing side wall 39 at evenly spaced locations, in a pattern generally evenly distributing the air ports over that portion of side wall 39 which is disposed opposite the reaction surface of the cathode assembly in the finished cell 10. Where 400 air ports are used, each air port is e.g. .015 inch nominal diameter, with a preferred range of about .010 inch to about .025 inch.

[0251] Larger or smaller numbers of air ports can be used depending on the use which is expected to be made of the cell. A larger number of relatively smaller air ports is preferred where greater limiting current is desired and where moisture vapor movement into or out of the cell is to be suppressed. Where the number of air ports is greater than 400, the average size of the air ports is preferably reduced in order to avoid excessive evaporation of electrolyte out of the cell, or ingress of moisture vapor into the cell. In general, as the sizes of the air ports are reduced, the overall open area of all air ports 38, taken in combination, can be reduced without reducing the limiting current of the cell, but beneficially reducing the overall rate of evaporation of electrolyte vapor from the cell or ingress of moisture vapor into the cell.

[0252] Where the number of air ports is less than 400, the average size of the air ports is increased, in order to compensate for the smaller number of air ports, and thus to provide sufficient oxygen at the reaction sites on the cathode to sustain the desired level of electrical power production. In general, as the sizes of the air ports are increased and the number of air ports is decreased, the overall open area of all the air ports 38, taken in combination, should be increased in order to maintain the limiting current of the cell. However, the overall rate of evaporation of electrolyte

bottom wall 37, in producing the finished structure at the bottom of the cathode can.

[0264] FIGURE 20 represents further working of the bottom wall of FIGURE 19 by a forming process illustrated in FIGURE 20A. FIGURE 20 illustrates a central elevated platform 108, and downwardly depending inner wall 110 extending from platform 108 to the lowest extremity 112 of the bottom wall. Inner wall 110 and the lower portion 114 of side wall 39, in combination, define a recessed annular slot 116 at the base of the can pre-form.

[0265] Referring to FIGURE 20A, the can pre-form of FIGURE 19 is placed on a hollow cylindrical lower tool 113. Tool 113 is rigidly mounted to an underlying support (not shown). Bottom wall 37 of the pre-form is disposed upwardly. The open end of the pre-form is disposed in a downward direction. An upper tool 115 advances downwardly against bottom wall 37 as shown by arrow 117. As upper tool 115 advances down, tool 115 pushes bottom wall 37 into the open central portion of lower tool 113. Correspondingly, side wall 39 is drawn upwardly toward the bottom wall as suggested by arrows 119. Tool 115 is advanced a predetermined distance, then stopped. Tool 115 generally does not abut tool 113, not even through bottom wall 37, but rather operates inside the walls of tool 113.

[0266] The overall result of the advance of tool 115, against the fixed support of can 28 by tool 113, is inward deformation of bottom wall 37 to form platform 108 and slot 116. Platform 108 and slot 116, and downward-most movement of tool 115, are illustrated in dashed outline in FIGURE 20A.

[0267] After formation of slot 116, air cathode assembly 26 is inserted into the slot, as illustrated in dashed outline in FIGURE 20. When the air cathode assembly is disposed in slot 116, inner surface 60 of current collector 32, at imperforate bottom edge portion 44, is disposed against the nickel layer on the corresponding interior surface 118 of wall 110. See also FIGURE 3A.

[0268] The facing surfaces 60 and 118 form the contact surfaces whereby electrical energy transported to and from the air cathode assembly is transferred to and from cathode can 28. In order to implement such energy transfer, the contact surfaces 60, 118 are brought into intimate electrical contact with each other in such manner as to maintain such intimate contact throughout the life of the cell. Such intimate contact is generally developed by urging surfaces 60, 118 toward each other, either directly or indirectly.

[0269] Referring to FIGURE 21, a forming tool (not shown) is inserted into the opening 120 above extremity 112 and below platform 108. The forming tool is turned about the circumference of inner wall 110, at the top of the inner wall and preferably against a supporting tool on the outer surface of lower portion 114 of side wall 39, thus to urge interior surface 118 of inner wall 110 against surface 60 of the current collector. As interior surface 118 is urged against surface 60, a bottom seal groove 122 is formed in inner wall 110. The recited forming of bottom seal groove 122 urges surface 118 of wall 110 into forced contact with inner surface 60 of current collector 32 thus to make the desired intimate physical and electrical contact.

[0270] In the alternative, instead of the forming tool being turned about the circumference of the can, groove 122 can be made by holding the forming tool stationary and turning the circumference of inner wall 110 about the forming tool.

[0271] In addition to established electrical contact with the current collector, the forcing of inner wall 110 against the air cathode, thus crimping inner wall 110 against the air cathode assembly, also traps or otherwise fixes the air cathode assembly in its specified especially longitudinal assembled position in the cell as well as generally defining its position with respect to the remaining elements of the cell. In addition, the crimping of inner wall 110 against the air cathode assembly also urges the air cathode assembly against the lower portion 114 of side wall 39, thus closing off any free path of travel for escape of electrolyte from the cell through slot 116. It may be noted by comparing FIGURES 20 and 21 that inner wall 110 of FIGURE 21 has a lower height than the corresponding wall 110 of FIGURE 20. The height of such wall 110 is thus adjusted depending on the ultimate configuration anticipated for the bottom structure of the cathode can.

[0272] FIGURE 22 illustrates a bottom structure much like the structure of FIGURE 21, but with a higher height for inner wall 110 between the lowest extremity 112 and platform 108, and wherein bottom seal groove 122 is intermediate the upper and lower ends of wall 110. The advantage of the embodiment of FIGURE 22 is that a wider variety of forming tools can be used to fabricate bottom seal groove 122. The respective advantage of the embodiment of FIGURE 21 is that the height of inner wall 110, and thus of opening 120, is smaller than in FIGURE 22, whereby the length of anode cavity 137, and the respective contained volume inside the completed cell 10, are correspondingly increased. The increased contained volume can be filled with additional anode mix 20 thus providing a potentially longer cycle life in the cell of FIGURE 21 compared to the cell of FIGURE 22.

[0273] FIGURE 23 shows another embodiment derived from the embodiment of FIGURE 22. In FIGURE 23, and after fabrication of bottom seal groove 122, platform 108 of FIGURE 22 has been urged downwardly such that bottom surface 124 of platform 108 is at the same height as bottom surface 126 of extremity 112. The result is a contained volume, inside the completed cell, even greater than the contained volume of the embodiment of FIGURE 21.

[0274] Referring back to FIGURE 19, FIGURE 24 represents an embodiment wherein no further fabrication is done to the bottom of the can prior to inserting the air cathode assembly into the can. Rather, the air cathode assembly is inserted into the can shown in FIGURE 19. Next a conductive inner plug 128, for example in the shape of a disc, is

## THE SEPARATOR

[0285] Separator 16 is positioned generally between air cathode assembly 26 and anode mix 20. Separator 16, in combination with bottom wall 98 of the cathode can and grommet 18, thus defines anode cavity 137 (FIGURE 32). The overall function of the separator is to maintain physical and electrical separation between anode mix 20, in the anode cavity, and the air cathode assembly. While maintaining the recited physical and electrical separation, separator 16 is required to enable facile passage of electrolyte, especially hydroxyl ions, therethrough, between the anode cavity and the air cathode assembly.

[0286] Suitable materials for making separator 16 are, for example, a tightly woven nylon web, a microporous polypropylene web, a nonwoven polypropylene web or a cellulosic web. The separator can be coated with a suitable ion exchange resin. An exemplary material is Acropor, NFWA from Gelman Sciences, a resin-coated woven nylon cloth. In addition, any separator material known to be suitable for use in an alkaline  $Zn/MnO_2$  cell can be used in cells of the invention, so long as the resulting separator has suitable porosity to pass electrolyte and hydroxyl ions while being generally impervious to passage of anode material and electric current. In general, preferred separator webs are coated on at least one surface with at least one of a number of well-known ion exchange resins.

[0287] The parent web from which the separator is ultimately fabricated is generally about .001 inch to about .005 inch thick, with preferred thickness of about .002 inch or about .003 inch. Such thicknesses and materials are well known in the art. Any separator material, of any thickness, generally known for use in alkaline electrochemical cells, can be used in cells of the invention.

[0288] Individual separators 16 are fabricated by cutting appropriate sized, e.g. rectangular, work pieces from a larger parent web. Such work pieces are sized such that a length or height dimension of the separator can extend from the bottom of the cathode can, above slot 116, (FIGURE 3A) to generally the top of the cathode current collector (FIGURE 3B). Width of the separator work piece is sufficiently great to extend about 1.25 to about 1.5 times around the circumference of the inside surface of the air cathode assembly.

[0289] During cell assembly, separator 16 is positioned against the air cathode assembly, preferably in surface-to-surface relationship with the air cathode assembly over the entirety of that portion of the inner surface of the air cathode assembly which extends above slot 116.

[0290] In generally preferred embodiments, the separator is not adhered or otherwise bonded to the air cathode assembly. Experiments have shown that cells fabricated with the separator unbonded to the air cathode assembly by e.g. an adhesive which is a combination of carboxymethyl cellulose and polyvinyl acetate, or the like. Thus, the inventors contemplate that normally-used adhesive may interfere with movement of the reacting ions in the cell especially at high rate demand levels.

[0291] Accordingly, in assembling a separator work piece into a cell, the separator work piece is generally formed into a cylindrical shape, with side edges overlapped. The cylindrically-shaped work piece is inserted into the cavity defined inside air cathode assembly 26, and optionally inside the cathode can, preferably without placing any adhesive on the separator for bonding the separator to the cathode assembly. The separator work piece is then released inside the air cathode assembly. The natural resilience of the separator work piece material causes the work piece to expand outwardly against the inner surface of the current collector. The natural resilience of the separator work piece then holds the separator work piece in place while additional elements of the cell are installed and secured in the cell.

[0292] On the other hand, if a gas bubble should occur at separator 16, such as between separator 16 and air cathode assembly 26, the cell output rate is reduced at high rate demands, and the overall cell output at high rate is reduced. Accordingly, in some embodiments where high rate demand is not a controlling issue, the separator can be adhered to the cathode current collector.

## THE BOTTOM ISOLATION CUP

[0293] As illustrated in FIGURE 3A, a bottom seal member such as bottom isolation cup 142 can be disposed on the bottom of the anode cavity, in surface-to-surface relationship with the bottom wall of cathode can 28, between the positively-charged bottom wall and the negatively-charged anode material. Cup 142 has a bottom wall 144 disposed against central platform 108 of bottom wall 37 of the can, and a side wall 146 extending upwardly from bottom wall 144 and engaging against the inner surface of separator 16.

[0294] Side wall 146 of isolation cup 142 is formed while being inserted into the anode cavity by pushing an appropriately-sized circle of material through a forming tube (not shown) using a punch (not shown) which closely approaches the outline of the inner surface of the forming tube and the separator in the cell. The isolation cup is thus formed as part of the process of the circle of resiliently deformable material being pushed directly into the anode cavity of the cell, inside separator 16. Side wall 146 is thus formed and thereby engaged against separator 16, by the process of forming and placing isolation cup 142. In addition, the forming and placing of isolation cup 142 by the punch and forming tube

melted material, if desired.

[0307] In general, one or the other of the bottom isolation cup (FIGURE 2) or the bottom seal (FIGURES 21-23, 27, 29-30) are used as the bottom seal member in a given cell. Some embodiments use both the isolation cup and the bottom seal (FIGURE 3A). When plug 126 is used, the plug takes on the electrical properties of the bottom wall, whereby isolation cup 142, or seal 140, or both, are disposed between the anode material and the plug. Thus, in these embodiments, the plug functions as a portion of bottom wall 37.

[0308] FIGURE 29 shows an embodiment wherein isolation cup 142 is not used. FIGURE 3A illustrates the relationship of the seal to the isolation cup where the cup is used. As seen in FIGURE 3A, the isolation cup is disposed between bottom wall 37 and bottom seal 140, and covers the entire circumference of the top of joint 148. Thus, bottom seal 140 provides an additional barrier, e.g. at joint 148, to electrolyte traveling along the inner surface of the separator, downwardly around bottom edge 59 of the current collector, and the bottom edge of the diffusion member, and thence out of the cell at an air port 38. A first barrier is the above recited crimp of the can as at seal groove 130 or 130W at flange 138 against inner wall 110 through current collector 32 and air diffusion member 36. A second barrier is joint 148 between the separator and side wall 146 or isolation cup 142. The bottom seal 140 is thus a third barrier to electrolyte leakage at the bottom of the cell.

[0309] Bottom seal 140 can be made from any polymeric material having suitable dielectric properties, having suitable chemical tolerance for the alkaline environment inside the cell, and having a melting temperature to accommodate placement and melting of the seal material in the cell without deleterious distortion of any of the other materials in the cathode can at the time the seal material is introduced into the can and distributed by heating.

[0310] As used herein, "melting temperature" refers to that minimum temperature where the polymer as a whole is subject to fluid flow. Such definition allows for unmelted included particles so long as the melt phase is the continuous phase.

[0311] While no minimum melting temperature is contemplated, materials found to have the properties described above generally have melting temperatures of at least about 350 degrees F., for example linear low density polyethylene.

[0312] At the upper end of the range, melting temperatures are acceptable in some embodiments up to about 650 degrees F. Above the recited upper end of 650 degrees F., the heat required to melt the respective seal material causes deleterious affect on at least one other element present in the cathode can when the seal material is melted in the can.

[0313] Thus, a wide variety of thermoplastic materials such as polyolefin and olefin copolymer compositions can be used for bottom seal 140. There can be mentioned as specific examples of such materials, without limitation, the low density polyethylenes, the ethylene vinyl acetates, the linear low density polyethylenes, mixtures and copolymers of the above materials, and the like.

## THE ANODE

[0314] Anode 12 includes electroactive anode mix 20, and anode current collector 22 centrally disposed and in intimate physical and electrical contact with the anode mix. Anode current collector 22 is held in position in the cell, and is electrically isolated from the cathode, by grommet 18.

[0315] The primary function of the anode is to react zinc metal with hydroxyl ions to thereby produce electrons according to the anode half reaction, the reaction correspondingly producing zinc oxide. The locus of such anode reaction is initially located adjacent the air cathode assembly in a fresh unused cell and, as the cell is used, the locus of reaction moves, generally as a reaction front, from the region of the cathode assembly toward the anode current collector.

[0316] FIGURE 31A illustrates a cell of the invention after significant discharge, and thus illustrates the general nature of the movement of reaction front 158. As seen in FIGURE 31A, the relatively less-densely stippled anode mix material 158, generally emanating inwardly from air cathode assembly 26, is reacted zinc oxide. The relatively more-densely stippled anode mix material 160, generally disposed about the lower portion of the anode current collector, is unreacted zinc.

## THE ANODE MIX

[0317] In general, anode mix 20 can be any anode mix that is known for use in a zinc electrochemical cell operating in an aqueous alkaline environment, and especially any anode mix used in an alkaline cell, including an alkaline air depolarized cell.

[0318] In general, such anode mix includes about 25% by weight to about 45% by weight potassium hydroxide, about 55% by weight to about 75% by weight particulate zinc, and suitable additives. Exemplary metal additives include bismuth, indium, cadmium, lead, and/or aluminum, as well as others known in the art. In a preferred embodiment, the additive package includes lead, indium, and aluminum. The indium is preferably present as indium compound in sufficient fraction to enable increased rate of electrochemical output of at least the anode portion of the electrochemical

[0332] In the above illustrated method of making anode material 26, the indium compound is added to the mixture after the organic surfactant is mixed with the particulate zinc.

[0333] An indium compound preferred for use herein is indium hydroxide. Methods of making suitable indium hydroxide are disclosed in United States Patent 5,168,018 Yoshizawa, and thus are well known.

5 [0334] When indium hydroxide powder is mixed with the particulate zinc, the indium hydroxide powder may coat the zinc particles. When the potassium hydroxide is added to the particulate zinc, part of the indium hydroxide may be electrodeposited onto the surfaces of the zinc particles through the principle of substitution plating, thereby raising the hydrogen overvoltage on the respective surfaces of the zinc particles. Any remaining portion of the indium hydroxide which is not so electrodeposited is believed to be retained in solid form in the alkaline electrolyte.

10 [0335] This "remaining portion" of indium hydroxide, if any, may be electrodeposited onto fresh surface of zinc exposed when the zinc is subjected to discharging, whereby the "remaining portion" of the indium can deposit on newly formed surface area of the zinc particles to thereby protect such newly formed surface areas from unwanted side reactions.

[0336] The smaller the particle size of the indium compound, the better the dispersion in the alkaline electrolyte, so that the indium compound can be effective uniformly throughout the anode mix. If the indium compound particle is too small, however, it may be immediately dissolved in the alkaline potassium hydroxide whereby the amount of the indium compound available to be used after partial discharge of the cell may be insufficient.

[0337] The potassium hydroxide need not have any additives, although use of the ZnO as indicated above is preferred. The optional use of ZnO discussed above is well known, so is not discussed further here.

20 [0338] The amount of potassium hydroxide can vary from a low of about 25% by weight of anode mix 20 to a high of about 45%. The balance of the anode mix is made up primarily of the particulate zinc, making allowance for the noted preferred additives. Preferred concentration for the potassium hydroxide is about 27% to about 40% by weight, with a most preferred concentration of about 30% to about 37% by weight of the anode mix.

[0339] The particulate zinc can generally be made from any battery grade zinc composition. Preferred particle size is about 100 to about 500 microns average, with at least about 90 weight percent of the zinc being within the stated range.

[0340] In a first series of embodiments of the anode material wherein dry zinc composition is placed in the anode cavity followed by addition of electrolyte, the zinc preferably includes a small amount of lead as an alloying agent, such as about 200 parts per million (ppm) by weight to about 1000 ppm by weight based on the weight of the particulate zinc. Preferred amount of lead is about 500 ppm by weight, or less. For use in the dry zinc addition method, indium preferably comprises no more than 5 ppm by weight of the particulate zinc alloy.

[0341] In the illustrated embodiments, the composition of the anode mix may include mercury as a functioning component therein. The amount of mercury can, however, be reduced as compared to conventional alkaline electrochemical cells. While an overall range of 0.0% by weight to about 12% mercury by weight is contemplated, preferred range for the mercury is up to about 3% by weight. A more preferred range is about 1% by weight to about 3% by weight mercury. Where suitable hydrogen overvoltage can otherwise be obtained, the preferred anode composition is free from effective amounts of mercury. However, where mercury is used, preferred particulate zinc is amalgamated such that the surface of the zinc bears an equivalent proportion of the mercury content to that of the bulk of the zinc.

40 [0342] While the precise mechanism is not fully understood, and while applicants choose to not be bound by technical theory here, applicants believe that mercury, where used, and in the presence of the indium and the organic surfactant, facilitates an increased electrochemical reaction rate capacity in the anode, thus releasing electrons from the zinc at an increased electrochemical reaction rate, enabling a faster discharge of the cell under high rate conditions.

[0343] The method of associating mercury with the zinc is not critical. Thus, mercury can be associated with the zinc as by physically mixing mercury with the zinc particles, by alloying mercury with zinc, by solution displacement reaction, and the like.

45 [0344] In the recently above noted embodiments, the particulate zinc alloy is preferably free from functionally detectable amounts of indium. To the extent the particulate zinc may comprise indium as an alloy component therein, the amount of indium alloyed with the zinc is generally less than 100 ppm by weight, based on the weight of the zinc.

50 [0345] It is believed that indium compound in the anode composition, separate from any indium alloyed in the zinc, provides a trigger mechanism enabling the desired high reaction rate in the anode mix. Conventional cells, on the other hand, exhibit steadily declining voltage under high drain rates, which suggests that the reaction rate of the electrochemical reactions in such cells is insufficient to maintain a constant voltage at high drain rates.

[0346] While the preferred embodiments have been described with respect to using indium hydroxide as the indium compound, indium chloride and indium sulfate are also contemplated to work as well, and so are within the scope of the invention. Applicants further contemplate that indium bromide, indium oxide, and indium sulfide, as well as other indium compounds, may work in place of the disclosed indium hydroxide.

55 [0347] Additional metal compounds contemplated to work, in addition to or in place of the indium compound, are compounds of cadmium, gallium, thallium, germanium, tin, and lead. Respectively, such compounds are CdO, Ga<sub>2</sub>O<sub>3</sub>,



and generally unreactive current collector 22.

[0361] The outer surface of shank 150 is finished to a desired uniform surface smoothness, and is preferably free of deviations from the general surface finish. Such deviations might be, for example, burrs, nicks, and scratches, which would add surface area and thus promote an unnecessary amount of gassing, especially where the surface of shank 150 may be plated with a gas suppressing plating material. Non-symmetrical current collectors can be used, provided accommodating modifications are made in cooperating ones of the other elements, for example grommet 18, with which the current collector interfaces and cooperates.

[0362] The anode current collector should efficiently collect current, and should conduct the current so collected to the anode terminal with minimal loss to internal resistance. Thus, in addition to the physical characteristics of the outer surface providing an efficient collector of electrical energy, the outer surface of the composition of current collector 22 should be a good conductor of electricity.

[0363] In general, known and commonly used current collectors incorporate large fractions of copper in their compositions because copper is a cost effective, good collector and good conductor, having low internal resistance. The particular composition selected for the anode current collector depends on the use anticipated for the cell, the environment in which the cell will be used, and the known efficiency of the materials under consideration, for collecting and conducting electricity under the anticipated use, and use environment, conditions. For primary cells, discharge capacity for a single discharge is a prominent consideration. Oxidation of the anode current collector, on the other hand, is of little concern so long as no oxidation occurs that would impede operation of the cell until after the cell is fully discharged.

[0364] Pure copper is generally not satisfactory for use as current collector 18, even under primary cell conditions. Accordingly, the copper is mixed or alloyed with additives, and/or the current collector is plated with, for example, tin, gold, or other oxidation suppressing plating material in order to obtain the desired collection and conduction properties in the current collector, without incurring unacceptable levels of oxidation of the current collector.

[0365] As suggested by the above noted plating, properties of collecting and conducting current are substantially controlled by the composition of the material at the outer surface of current collector 22. Accordingly, the current collector can comprise a substrate made of any of a variety of materials selected for other than current collecting or current conducting properties. Such substrate has the general size and shape desired for the finished current collector. The substrate material can be selected based on, for example, weight, cost, strength, or the like. The substrate is coated, such as by plating, cladding, or the like with an outer layer having desired properties associated with collecting and conducting electrical energy. The material used as the coating can also be used as the substrate, as in FIGURE 2, whereby the coating per se is obviated.

[0366] It is known to use, for example, a number of brass compositions in making current collectors, such as 50% by weight to 80% by weight copper, and respectively 20% by weight to 50% by weight zinc. Specific examples are 70% by weight copper and 30% by weight zinc, 65% by weight copper and 35% by weight zinc, 60% by weight copper and 40% by weight zinc, and 50% by weight copper and 50% by weight zinc. Such materials can be used as the entire mass of the current collector, or as a coating on an underlying substrate. Multiple effective coating layers can be used on a substrate so long as the electrically effective outer layer exhibits the desired collection and conduction properties.

[0367] The above-noted brass compositions are sufficiently effective at suppressing oxidation as to be acceptable for use in primary cells which employ a single discharge cycle before the cell is disposed of. In general, the higher the copper fraction, the lower the internal resistance in the current collector. Similarly, the lower the copper fraction, the higher the internal resistance. It is known to use an anode current collector composition having copper modified with up to about 11% by weight silicon, and generally comprising up to about 0.5% manganese, and the balance copper. A most preferred anode current collector is a brass substrate having about 60% by weight copper and about 40% by weight zinc, and plated with tin over the brass.

[0368] In general, the anode current collector is assembled to grommet 18 by pushing shank 150 through aperture 154 in the grommet. The combination grommet-current collector is then emplaced in the can, with concurrent driving of shank 150 of current collector 22 into zinc anode mix 20. This brings the shank into intimate electrical contact with the zinc anode mix.

#### THE GROMMET

[0369] Referring to FIGURES 3B and 18, in the embodiments illustrated, grommet 18 has a first major diameter 162, generally corresponding with the general inner diameter of the cathode can, an intermediate diameter 164, and a minor diameter 166. Ledge 106 defines a step diameter change between major diameter 162 and intermediate diameter 164. Ledge 168 defines an arcuate diameter change between intermediate diameter 164 and minor diameter 166. Central aperture 154 extends through the grommet, from top to bottom, and is operative to receive shank 150 of anode current collector 22 while excluding head 152, thus to present head 152 for electrical contact with either an outside circuit or anode cap 24 (FIGURE 2).

[0370] The functions of grommet 18 are generally as follows. First, the grommet provides cell closure at the top of

ance terminals are preferably structured to interface with head 152 on the anode current collector, and either platform 108 or flange 138 of the cathode can, obviating anode and cathode caps 24, 30. As a further option, platform 108 and head 152 can be so configured as to be disposed in the physical location and physical arrangement usually extant in conventional cells of the standard size of interest.

- 5 [0384] Anode cap 24 and cathode cap 30 can be fabricated from any conductive material which can readily make good electrical contacts, and which will tolerate the physical stresses which are typically placed on such caps during routine use of the cell. A variety of such materials can be used for caps 24, 30. One can use, for example, a wide variety of materials such as those recited for use in fabricating the cathode can. Among the materials which can be used for either or both of the anode cap and the cathode cap are, for example and without limitation, cold rolled steel, 10 optionally coated on one or both sides with nickel; and stainless steel such as 305 stainless steel, optionally coated on one or both sides with nickel. Other materials known in the battery art for use as electrode caps in alkaline round cells are equally useful in cells of the invention.

#### CORNER STRUCTURE DETAIL

- 15 [0385] FIGURES 3A and 3B, taken at dashed circles 3A and 3B respectively in FIGURE 2, represent enlargements of the top and bottom respectively of the interior structure of the cell at and adjacent the top and bottom of the air cathode. FIGURES 3A and 3B illustrate especially the seals, about the air cathode assembly at the top and bottom of cell 10, against electrolyte leakage, and in promotion of electrical isolation of the anode and cathode from each other.
- 20 [0386] Referring to, for example, FIGURE 7, any electrolyte traversing through the air cathode assembly must pass through the PTFE air diffusion member. However, the PTFE is hydrophobic, whereby the aqueous electrolyte generally does not traverse through the PTFE. Accordingly, the PTFE air diffusion member is effective in normal use to prevent aqueous electrolyte from passing through the PTFE and thence out of the cell.
- 25 [0387] The cell is especially vulnerable to leakage of electrolyte, however, at any location where the electrolyte can by-pass the PTFE, and traverse a path that does not require that the electrolyte traverse through the PTFE or along a surface of the PTFE. Such paths potentially exist at the top and the bottom of the cell adjacent the separator and the air cathode assembly. And while such paths devoid of such PTFE can be effectively sealed against electrolyte leakage, such seal paths are more difficult to seal than corresponding paths employing such PTFE.

#### CORNER STRUCTURE AT THE BOTTOM OF THE CELL

- 30 [0388] Referring to FIGURE 3A, inner wall 110 of bottom wall 37, and lower portion 114 of side wall 39 form the inner and outer walls of flange 138 at the bottom of the cell, thus at slot 116 on the interior of the cell. As discussed with respect to the bottom structure overall, cathode current collector 32 and air diffusion member 36 extend downwardly into slot 116.
- 35 [0389] As illustrated in FIGURES 21-24, the invention contemplates various implementations of crimping the flange in order to collapse slot 116 at various bottom seal grooves such as 122, 130, and the like, thereby to bring inner wall 110 and lower portion 114 of side wall 39 together in intimate relationships with the current collector and the air diffusion member, and into close proximate relationship with each other.
- 40 [0390] FIGURE 3A illustrates that carbon catalyst 34 need not, and preferably does not, extend into slot 116, but is confined between air diffusion member 36 and current collector 32 above slot 116. Similarly, the bottom edge of separator 16 extends generally to, but not into, slot 116. Thus, in preferred embodiments, the material extending into slot 116 is limited to the cathode current collector and the air diffusion member. As illustrated in FIGURE 3A, the air diffusion member is rather compressible, and is accordingly highly compressed in the area of crimped bottom seal groove 130W, and by its typical resilience, entirely fills any residual width of the slot with its hydrophobic composition.
- 45 [0391] Referring to the bottom of the cell and FIGURE 3A, liquid may potentially traverse a path downwardly to the bottom of slot 116, about the bottom edges of the cathode current collector and the air diffusion member, and upwardly along the outer surface of the diffusion member to an air port, thence to exit the cell. Points along such path are where separator 16 meets isolation cup 142 and where the bottom of separator 16 meets air cathode assembly 26, as well as the first choke region adjacent inner wall 110 at the wide bottom seal groove in slot 116 and the second choke region adjacent lower portion 114 of side wall 39 at wide bottom seal groove 130W.
- 50 [0392] Such path generally begins where separator 16 meets bottom seal 140, and passes between separator 16 and bottom seal 140; and/or the path traverses between separator 16 and isolation cup 142 along joint 148, thence downwardly past the bottom of separator 16, thence continuing downwardly between wall 110 and cathode current collector 32, through the first choke region at the wide bottom seal groove in slot 116. The path then traverses past the bottom end of the cathode current collector and around the end of the current collector and air diffusion member 36, to the outer surface of the air diffusion member. Once on the outer surface of the air diffusion member, the path traverses upwardly through the second choke region, namely past seal groove 130W between air diffusion member
- 55

36 to the top of the slot.

[0406] Any liquid which manages to get past the compressed hydrophobic diffusion member and thus through slot 174 and to ledge 168, depending on the path of interest, next encounters either the pressure between compressed wide sealing groove 176 and the compressed air diffusion member on the downwardly directed path, or encounters the pressure between the grommet and side wall 39 of the cathode can. Referring to the downwardly directed path, the pressure between wide sealing groove 176 and the hydrophobic air diffusion member constitutes a significant obstacle to traverse of aqueous electrolyte. In addition, in order to completely traverse wide sealing groove 176, the electrolyte must pass around or through seal ring 76 before advancing to an air port.

[0407] Referring to the upwardly directed path, upward of ledge 168, a grommet lock groove 178 in side wall 39 (FIGURE 2) preferably extends about the circumference of the cell between wide sealing groove 176 and the top of grommet 18. Grommet lock groove 178 is formed in can side wall 39 after the grommet has been installed in the can, and thus crimps the side wall of the cathode can against grommet 18 with sufficient pressure (i) to hold, or at least assist in holding, the grommet in the can and (ii) to block flow of electrolyte between grommet 18 and side wall 39 upwardly toward the top of the cell. Grommet lock groove 178 exerts sufficient ongoing active pressure against grommet 18 to substantially impede flow of liquid e.g. electrolyte upwardly past grommet lock groove 178. The crimping of grommet lock groove 178 is practiced specifically for, among other functions, creating such an obstacle to flow of liquid electrolyte.

[0408] For effective leakage prevention, wide sealing groove 176 substantially closes slot 174 except for the width required by the combination of the cathode current collector, and the two layers of the highly compressed air diffusion member. The deformation properties of the e.g. cold rolled steel core layer of side wall 39 of the cathode can are such as to maintain the deformation of groove 176 as imposed at the crimping step, thereby to maintain slot 174 closed to traverse of liquid electrolyte after the crimping force of the respective tooling is released.

[0409] Wide sealing groove 176, as illustrated in FIGURES 2 and 3B is fabricated by placing a grooving tool in the existing grommet stop groove 102 (See also FIGURE 30) and working the tool about the circumference of the can as well as downwardly, thus using the tool to widen the existing groove downwardly such that the groove extends continuously downwardly from the stop groove, and continuously about the circumference of the can. Thus, the height of the comparatively wider sealing groove 176 incorporates, and expands on, the original rather narrower stop groove 102.

[0410] In another embodiment, illustrated in FIGURE 30, a separate top sealing groove 180 is fabricated in side wall 39 below grommet stop groove 102 and above the bottom of slot 174. Such top sealing groove 180 performs generally the same function as wide sealing groove 176, but over a lesser height of the cell, and separate from stop groove 102.

[0411] In yet another embodiment, not shown, of corner structure at the top of the cell, namely adjacent the top of anode cavity 137, but referring for guidance to FIGURE 3B, diffusion member 36 extends upwardly into slot 174 and terminates at a top edge adjacent the corresponding top edge of cathode current collector 32. Namely, in this embodiment, diffusion member 36 is not turned inwardly and downwardly inside the cathode current collector between the cathode current collector and grommet 18. Rather, cathode current collector 32 is in direct surface-to-surface relationship with grommet 18.

[0412] While the separator is generally wettable by aqueous liquids, the pressure at e.g. wide sealing groove 176 is effective to at least partially suppress migration of aqueous liquid upwardly into slot 174 in those embodiments where separator extends upwardly into slot 174. Thus, while the separator is generally hydrophilic, under the pressure of sealing groove 174, the separator loses at least part of its hydrophilic characteristic properties, and serves as the first line of defense against leakage of liquid electrolyte out of the cell. Any liquid electrolyte which does manage to get past the separator in the slot, still must traverse the choke points and other obstacles in one of the upwardly and downwardly directed paths described earlier herein, in order to effectively leak out of the cell.

#### SEALING TAPE

[0413] As with other air depolarized electrochemical cells, a seal tape, suggested in dashed outline at 182 in FIGURE 1, is installed on the outside surface of the cathode can, covering the air ports. In the cylindrical embodiments of cells of the invention, the sealing tape is installed about the entire circumference of the outer surface of side wall 39 and preferably extends from proximate e.g. bottom seal groove 130 to a location generally proximate sealing groove 176 or 180, as applies. Tape 182 covers air ports 38, and blocks unrestricted access of air to the air ports, until such time as the cell is to be placed into service. When placement of the cell into service is imminent, the tape is removed, thereby exposing the air ports to ambient air, whereby the cathode half reaction is facilitated.

[0414] Seal tape 182 can be made from any of the seal tape materials known for use over air ports of air depolarized cells. Preferred materials are those known for use where chemical reactions are suitably suppressed, for lack of air, until such time as the cell is to be placed into service.

[0415] Such material can have, for example, a 2 inch wide base web about .002 inch thick and with suitable known porosity, with e.g. suitable pressure sensitive adhesive mounted thereon. The tape is applied by wrapping a suitable

are used, for any electrolyte to get through the diffusion member, the electrolyte must either traverse through the thickness of 3 layers of the PTFE (not likely), or traverse along facing surfaces of adjoining layers of the PTFE for 3.25 times the circumference of the diffusion member (again not likely). Given the above obstacles to liquid egress from the cell, liquid electrolyte in general does not exit the cell through the PTFE diffusion member. Thus, the multiple layer  
 5 endless wrap structure of the PTFE diffusion member is a significant factor in impeding such liquid exit through the diffusion member.

[0426] In technically preferred embodiments, the diffusion member is turned inwardly about the circumference of the cell, over the top of the separator or cathode current collector, and downwardly onto the top portion of the inner surface of the respective cathode current collector or separator. The downwardly-depending portion of the PTFE on the inner  
 10 surface of the cathode current collector or separator provides a first-encountered sealing shield, in slot 174, impeding movement of electrolyte or electricity from anode mix 20 to the cathode current collector or the cathode can, thus impeding internal electrical shorting in the cell.

#### OVERALL METHOD OF MAKING A CELL

15 [0427] The following materials are provided for assembly of a cell of the invention. A cathode can as described above is provided. Such cathode can has air ports 38 in side wall 39, in suitable number, preferably evenly distributed over side wall 39 adjoining the prospective reaction surface area of the air cathode assembly. The cathode can includes provision for stabilization of the bottom of the air cathode assembly as at either slot 116 or through plug 128, or the  
 20 like, optionally in combination with groove 122 or 130. The cathode can preferably further includes grommet stop groove 102.

[0428] An air cathode assembly 26 as described above, is provided. In such air cathode assembly, an upstanding free edge region of the PTFE diffusion member preferably extends e.g. about .050 inch to about .150 inch, preferably about .100 inch to about .125 inch, above the top of the cathode current collector.

25 [0429] A grommet 18 is provided, including ledge 106 properly positioned for interfacing with grommet stop groove 102. Either grommet stop groove 102 or ledge 106, or both, can be continuous as shown, or can be intermittent about the circumference of the can and grommet. The only requirement is suitable interface to stop advance of the grommet as the grommet is assembled into the cell.

[0430] A separator 16 as described above is provided. The height of the separator is such as to extend generally from the top of slot 116 or plug 128 to and into what will become slot 174 between grommet 18 and side wall 39 of the cathode can. The width of the separator is sufficient to extend more than the full circumference of the anode cavity. The composition of the separator is preferably as described above, though a wide variety of known separator materials can be tolerated in the invention. The thickness and resiliency of the sheet material used to make separator 16 is such as to anticipate a resilient expansion of a lightly coiled such material inside the air cathode assembly when the lightly  
 30 coiled material is released inside the cathode can.

[0431] A suitable anode mix or anode mix precursor is provided. The anode mix is preferably the above described wet anode mix, preferably made as described, with the electrolyte composition being incorporated with the dry powder prior to the anode mix being incorporated into the cell. However, a wide variety of known anode mixes, including dry anode mixes, subsequently wetted inside the anode cavity, can be used in cells of the invention; and a wide variety of  
 40 known operable methods of making such anode mixes, are acceptable, and operable in making cells of the invention, although the above described anode mixes are preferred. The reason such anode mixes are preferred is because such anode mixes can potentially provide higher discharge rates than other, more widely-used anode mixes.

[0432] A suitable anode current collector is provided. While a wide variety of anode current collectors can be used, a preferred anode current collector for some embodiments is a brass nail (70% copper, 30% zinc) in the form of a solid rod, coated (e.g. plated) with tin, gold, or other material providing a sufficiently high hydrogen overvoltage to impede  
 45 self-generation of hydrogen gas inside the environment extant in the cell.

[0433] A suitable bottom seal material 140 is provided. The bottom seal material can be provided in either solid or melted/liquid form, depending on the method which is to be used in placing the seal material into the cell. When the seal material is provided in melted form, the melted material is generally contained in suitable spray machinery, including  
 50 a suitable reservoir, a spray nozzle, and a pump for pressurizing the melted seal material. When the seal material is provided in solid form, preferably a single pellet of suitable weight (e.g. 0.25 gram for a size "AA" cell) is provided. Multiple pellets, of suitable combined mass, for use in a single cell are acceptable, but less desirable.

[0434] Given the above provided materials, air cathode assembly 26 is inserted into the cathode can, with the bottom of the air cathode assembly extending to the inside surface of the lowest extremity 112 of bottom wall 37.

55 [0435] The bottom wall of the cell is then crimped, either at flange 138 or against a conductive plug 128, using a groove e.g. 122 or 130, thus to fix air cathode assembly 26 in position in the can to provide electrical contact between the cathode current collector and the cathode can, and to effect a seal impeding flow of electrolyte around the lower end of the cathode assembly and thence out of the cell.

aperture 154.

[0448] The subassembly of the grommet and the anode current collector is then inserted into the anode cavity, with the shank of the current collector disposed inwardly of the grommet, and penetrating into, and into intimate physical and electrical contact with, the anode mix. The grommet/current collector subassembly is preferably advanced into the anode cavity until grommet ledge 106 abuts ledge 104 of stop groove 102 of side wall 39 of the cathode can.

[0449] After the grommet and anode current collector are inserted into the cathode can, suitable grooves are formed or expanded about the side wall of the cathode can to lock the grommet in place, and to provide effective seals against leakage of e.g. electrolyte out of the cell past grommet 18. For example, the cell can be turned against suitable tools to create grommet lock groove 178 (FIGURE 30) and/or top sealing groove 180, or both (FIGURE 30), about the entire circumference of side wall 39. Grommet lock groove 178 is optional. Top sealing groove 180 is obviated where grommet stop groove 102 is expanded downwardly as shown in, for example, FIGURES 2 and 3B to form wide grommet lock groove 176, generally extending between and including what are shown as stop groove 102 and sealing groove 180 in FIGURE 30.

[0450] Inserting grommet 18 and anode current collector 22 into the can, and forming the recited grooves 176, 178, 180, as appropriate, completes the closure of the cell, including forming a desirably tight closure and seal of the cell.

[0451] Wide sealing groove 176 is fabricated by placing the working tool into grommet stop groove 102, and holding the tool at a suitable radius to provide inwardly-directed sealing force against grommet 18 while turning the cell and gradually moving the working tool downwardly from the height of stop groove 102. As the tool is moved gradually downwardly while holding the recited radius, stop groove 102 is expanded downwardly and optionally inwardly, thereby to bring pressure to bear against the diffusion member, cathode current collector, and separator, and indirectly against grommet 18, over an expanding vertical height eventually reaching the dimension "H1" (FIGURE 3B) and locking the diffusion member, the cathode current collector, and separator in a press-fit configuration in slot 174, against grommet 18, thus to form the wide grommet lock groove as illustrated in FIGURES 2 and 3B.

[0452] Height "H1" of wide grommet lock groove 176 is substantially greater than the height of grommet stop groove 102 illustrated in e.g. FIGURES 18 and 31. Typical ratio of the height "H1" of grommet lock groove 176 to the height of grommet stop groove 102 is of the order of about 2/1 to about 10/1, with preferred ratio of about 4/1 to about 8/1.

[0453] With suitable sealing grooves and/or locking grooves having been formed in side wall 39, the cell is at that point adequately closed and sealed against leakage of contents of the cell. Top edge 177 of the cathode can is then crimped inwardly, along with top ridge 172 of the grommet, against the top surface of the grommet, thereby to provide the final closure crimp in closure of the cell.

[0454] If an anode end cap 24 is to be used, the anode end cap is placed against the top of the grommet before the top edge of the can and top ridge of the grommet are crimped over. In such event, the circular outer perimeter of the anode cap is thus trapped in slot 170 as the top edge of the can and the top ridge of the grommet are crimped over, holding the anode cap to the anode end of the cell. The anode cap is electrically isolated from top edge 177 of cathode can 28 by the intervening electrically insulating top ridge 172 of the grommet.

[0455] While the anode cap is thus placed in close, and likely touching, proximity with head 152 of the anode current collector, a spot weld is preferably formed between head 152 and cap 24, thus to establish excellent electrical contact between the anode current collector 22 and anode cap 24.

[0456] Correspondingly, if a cathode cap 30 is to be used, the cathode cap is placed against preferably the lowest extremity 112 of the cathode can, and welded in place, thereby to obtain physical securement of the cathode cap to the cathode can and to establish excellent electrical contact with the cathode can.

#### HOLLOW ANODE CURRENT COLLECTOR

[0457] FIGURES 31A and 31B represent cross-sections of representative cells after significant discharge of the respective cells. FIGURE 31A represents a cell having an anode wherein the zinc was placed in the anode cavity in the dry condition, with the electrolyte having been added to the anode cavity after addition of the dry zinc.

[0458] By contrast, FIGURE 31B represents a cell having an anode wherein the zinc was placed in the anode cavity in the wet condition. Namely, the electrolyte was added to, and mixed with, the zinc before the zinc was placed into the anode cavity.

[0459] Both of FIGURES 31A and 31B illustrate movement of reaction front 156 of the anode half reaction as oxygen from the air combines with the zinc in the anode, through the auspices of hydroxyl components of the electrolyte. As illustrated therein, the relatively lighter colored anode mix material 158, namely the reacted zinc oxide, generally emanates inwardly from air cathode assembly 26. The relatively darker colored anode mix material 160, namely the unreacted zinc, is generally disposed relatively inwardly in the cell, about the anode current collector.

[0460] As FIGURES 31A and 31B illustrate generally, in a fresh, unused cell, being put into use for the first time, the anode half reaction between hydroxyl ion and zinc initially takes place immediately adjacent the air cathode assembly. Thus, the reactive hydroxyl ion reacts with one of the first available zinc particles it encounters as it leaves the cathode

the ratio of energy to weight is favorably advanced.

[0472] Thus, as diameter "D1" of hollow shank 150 is increased, the amount of unreacted zinc existing in the cell after full effective discharge of the cell is decreased until the shank is sufficiently large, thus sufficiently close to the separator, that substantially all the zinc is consumed by the time the cell reaches the end point voltage, of typically about 0.9 volt to about 1.0 volt. Namely, the greater the diameter "D1," the closer is side wall 184 to separator 16, and thus the less the distance between shank 150 and separator 16.

[0473] In comparing variations of the embodiments represented by FIGURE 32, and in light of the teachings respecting FIGURES 31A, 31B, and further assuming that the diameter of the shank does not extend outwardly beyond the reaction front represented in e.g. FIGURE 31B, the closer side wall 184 of shank 150 comes to separator 16, the less the amount of unreacted zinc at the end point. Where the ratio of total energy to weight is an important operational criterion of the cell, the preferred construction is a cell having no, or substantially no, unreacted zinc at the cell end point, namely when the cell can no longer provide the threshold required voltage at the effective load. Accordingly, the diameter of shank 150 preferably corresponds generally with the diameter of the reaction front when the end point voltage of the cell is reached.

[0474] In that regard, compared to an anode current collector having a solid shank, improvement in the energy/weight ratio is seen at any time when the expanded diameter of shank 150 displaces what would otherwise have been unreacted zinc at the end point of the use life of the cell. Accordingly, some benefit is usually seen when the distance between side wall 184 and separator 16 is no more than 40 percent of the average distance across the diameter, or other cross-section, of anode cavity 137. Depending at least in part on width "W5" of anode cavity 137, further improvements are seen in the energy/weight ratio in cells wherein the distance between side wall 184 and separator 16 is less than 40 percent of the average distance across the diameter. Thus, a distance of no more than 30 percent typically provides an improvement over the 40 percent distance.

[0475] A still further improvement is typically obtained when the distance is no more than 25 percent. Yet further improvement is seen in at least some embodiments when the distance is no more than 20 percent. In some embodiments, still further improvements are seen when the distance is no more than 15 percent, or 10 percent. The actual optimum percentage depends on a variety of parameters relating to the specific cell under consideration. Such parameters can include, for example, size and configuration of the anode cavity, the wet or dry condition of the zinc when placed in the anode cavity, end point voltage, drain parameters including drain rate, and the like.

[0476] As used herein, "average distance across the diameter" means the average distance taken across the cross-section of the cell, and wherein diameter is the diameter of a cell having the same cross-sectional area as the specific cell being evaluated. Thus are cells having non-cylindrical configurations provided for, as well as cylindrical cells.

[0477] Once the expanded diameter of shank 150 reaches the point where no substantial mass of unreacted zinc as at 160 remains when the cell reaches the end point, namely the diameter of the shank corresponds with the reaction front at the end point, any further reduction in the distance between shank 150 and separator 16 does not significantly further improve the energy/weight ratio, whereby the average distance between the tubular anode current collector and the separator is sufficiently small that substantially no unitary unreacted mass of zinc remains proximate the anode current collector when the cell reaches typical end point voltage of about 0.9 volt to about 1.0 volt. Where the reaction front is not parallel to shank 150, the optimum diameter is somewhat less than where the reaction front is parallel to shank 150, and a corresponding adjustment in the designed cross-section of shank 150 is preferred.

[0478] Still referring to FIGURE 32, side wall 184 and end wall 186 of shank 150 define cavity 188 inside shank 150. Cavity 188 can be open to ambient atmosphere through port 189 in head 152 of current collector 22. Accordingly, any pressure imposed on shank 150 which translates to a dimensional change in e.g. diameter of shank 150 results in a corresponding ingress or egress of air into or out of cavity 188 through port 189. Correspondingly, cavity 188 is not open to anode cavity 137, which would obviate the pressure moderating effect of port 189.

[0479] Side wall 184 can be defined by a suitable material have a suitable thickness "T3," for example and without limitation, about .006 inch to about .020 inch, defining a structural strength in shank 150 such that shank 150 withstands forces typically exerted inside anode cavity 137. Such forces represent, for example, the increased volume requirement of the anode material as the zinc is converted to zinc oxide in the electrochemical reaction. Such suitable material can be any of the brass compositions conventionally used for anode current collectors in cells having alkaline environments, for example, brass having compositions of 70 percent copper 30 tin, or 60 copper 40 tin. Other brass compositions, as well as other conventional anode material compositions, can be used as desired. The composition requirements are only limited by the suitability of the material for use as a current collector in the alkaline e.g. potassium hydroxide environment. Various material compositions are known for use in such alkaline environments, and all such materials are contemplated for use in the instant invention.

[0480] In other embodiments, thickness "T3" is selected, along with suitable material, to be thinner, for example and without limitation, about .002 to about .020 inch thick, such that shank 150 collapses under forces typically extant in the anode cavity during typical conditions to which the cell is exposed. While the same materials as above can be used, e.g. the thickness of side wall 184 is reduced, whereby the side wall of the shank which passes through grommet

TABLE 3 (continued)

Ex. No.	Discharge Current	Current per Cathode Area	hr to 0.9V Best of 5 cells	Ahr to 0.9V Best of 5 Cells
3C	1 Amp	135 mA/cm <sup>2</sup>	1.0	1.0
4C	.05 Amp	7 mA/cm <sup>2</sup>	46.0	2.3

Referring to Table 3, Examples 1 and 2 represent cells of the invention. Examples 3 and 4 represent conventional cells "Best of 5 cells" means that 5 cells were tested, and the number reported was the best cell of the 5 tested.

[0493] Table 3 shows that cells of the invention have distinct advantage over same-sized conventional alkaline manganese cells.

#### CAN-LESS CELL DESIGN

[0494] FIGURES 33 and 34 illustrate yet another set of embodiments of cells of the invention, wherein the cathode can per se has been deleted as a receptacle for receiving and containing the remaining elements of the cell, and structural strength of the cell is provided by other cell elements. To that end, the cathode current collector is preferably .007 inch thick instead of the 0.005 inch thickness indicated for the previous embodiments which do include a cathode can. A top e.g. closure member is used to consolidate the cell elements at the top of the cell. A bottom e.g. closure member is used to consolidate the cell elements at the bottom of the cell.

[0495] FIGURES 35 and 36 illustrate first and second apparatus and methods for assembling the top and bottom closure members with the remaining elements of the cell.

[0496] Finally, FIGURES 37 and 38 illustrate embodiments of the can-less cells employing hollow anode current collectors.

#### BASIC CAN-LESS CELL DESIGN

[0497] Referring now specifically to FIGURES 33 and 34, cathode assembly 26 is configured and assembled as in the above described embodiments except that a thicker cathode current collector is used. Preferred cathode current collector is 0.007 inch thick, thereby providing additional hoop strength to the cathode assembly. Cathode assembly 26 is made in the manner described above, making allowance for the thicker current collector material.

[0498] Annular top closure member 200 receives the top end of the cathode assembly, while annular bottom closure member 202 receives the bottom end of the cathode assembly. Anode current collector 22 is received through top closure member 200 and projects into the anode mix as in the earlier embodiments.

[0499] Top closure member 200 includes a slimmed-down nylon grommet 204 received in a metal contoured top washer 206. Grommet 204 receives anode current collector 22 through central aperture 154. Contoured top washer 206 includes an outer annular slot 208 which receives an annular member 210 of grommet 204, the grommet having a corresponding annular slot 211, whereby the combination of slots 208, 211 define an annular receptacle receiving the top edge region of the cathode assembly.

[0500] FIGURE 34A illustrates another embodiment of the can-less, receptacle-less structure, wherein the illustration shows the cell immediately prior to crimping of the top closure member inwardly in final closure of the cell. As shown, grommet 204 is constructed with a substantial angle  $\beta$  in slot 211, of about 2 degrees to about 90 degrees, preferably about 5 degrees to about 30 degrees, more preferably about 5 degrees to about 20 degrees. Thus, slot 211 is quite open at the bottom to receive cathode assembly 26. Angle  $\beta$  is defined by upwardly extending leg 210A, outer flange 210B, and downwardly depending leg 210C, of annular grommet member 210. Top washer 206 is placed over the grommet, whether before or after the grommet is assembled to the cathode assembly. Final crimping of top washer 206 inwardly against leg 214, accordingly, also substantially collapses angle  $\beta$  of the grommet while closing slot 211 and crimping leg 212 against the side of the top closure structure.

[0501] FIGURE 34A further illustrates in dashed outline that leg 210C can initially extend outwardly from flange 210B. In such case, leg 210C is pushed downwardly when top washer 206 is assembled to the grommet, to the position shown for leg 210C in solid outline in FIGURE 34A.

[0502] FIGURE 34B illustrates a further embodiment of the can-less receptacle-less structure, as in FIGURE 34A, but without downwardly extending leg 210C. Rather, annular member 210 ends at the outer edge of outer flange 210B approximately in line with the outer surface of diffusion member 36. In this embodiment, outer leg 212 of washer 206 is crimped directly against the outer surface of the diffusion member. Thus, in this embodiment, diffusion member 36 takes on an additional function of providing electrical insulation between top washer 206 and cathode current collector 32.

[0503] FIGURE 34C illustrates a yet further embodiment derived from the structure of FIGURES 34A and 34B, and

leakage of electrolyte out of the bottom of the cell. Finally, joining the bottom closure member to the cathode assembly generally defines a receptacle for receiving the anode material.

[0515] With the bottom closure member joined with the cathode assembly, and sealed to the bottom of the cathode assembly, the subassembly is then placed in an upright disposition, with the top of the cathode assembly extending upwardly to define a generally open receptacle.

[0516] Next the separator is inserted in the manner described earlier. The separator material and structure can be that of any of the separators described earlier. After the separator has been inserted, either or both of isolation cup 142 and/or seal 140 are inserted into the open receptacle to finish defining the interior of the anode cavity. The anode mix is then placed in the cell, either a wet anode mix or the 2-step addition of a dry anode mix as described earlier herein.

[0517] With the anode mix in place, the top closure member, including the anode current collector, is placed on the top of the cathode current collector, correspondingly inserting the anode current collector into the anode mix. The combination of top closure member 200 and anode current collector 22 is then crimped in place to thereby seal the cell. Inserting the anode current collector into the anode mix establishes electrical contact between the anode mix and the anode terminal at head 152 of the anode current collector. The crimping of the top closure member to the cathode current collector closes the cell to leakage of electrolyte out of the cell.

[0518] Top and bottom closure members 200, 202 can be crimped to the cathode assembly at the above respective steps using apparatus such as that illustrated in FIGURE 35. Referring to FIGURE 35, a spring-mounted holder 228 receives the top end of the cathode assembly, and supports the top end while the bottom end of the cathode assembly is disposed upwardly in the apparatus shown.

[0519] Bottom closure member 202 is then placed on the upwardly-disposed bottom end of the cathode assembly. A slotted, cone-shaped collet 230 is then advanced downwardly onto the bottom closure member and against conically-shaped female tooling 231, simultaneously clamping downwardly and inwardly on the bottom closure member. An inner supporting tool 232 provides support to inner leg 226 while collet 230 crimps inwardly on leg 224, thereby to establish crimped electrical contact between the cathode current collector and bottom closure member 202 at leg 226. The crimp closure also crimps the cathode assembly against seal member 220, thus establishing the seal against leakage of electrolyte out of the cell about the bottom edge of cathode assembly 26.

[0520] With the bottom closure member thus secured to the bottom of the cathode assembly, the subassembly is then turned right-side-up, with the bottom of the cell being disposed downwardly. The separator is then inserted into the subassembly, followed by isolation cup 142 and/or seal 140 to thereby complete the definition of the anode cavity. Then, the anode mix is placed in the anode cavity. With the anode mix in place, the subassembly of top closure member and anode current collector is then assembled to the cathode assembly and the bottom closure member. Accordingly, the anode current collector is inserted into the anode mix and the top closure member is seated on the top of the cathode assembly such that the top of the cathode assembly is received in slot 211.

[0521] The above described assemblage is then placed in holder 228 of the closure apparatus illustrated in FIGURE 35, with the bottom closure member being received in holder 228 and the loosely assembled top closure member extending upwardly therefrom. Collet 230 is then brought down onto top closure member 200, crimping outer leg 212 of the top closure member downwardly and inwardly while supporting tool 232 supports inner leg 214 in channel 236 of top closure member 200.

[0522] The crimping process practiced in the working of FIGURE 35 in general provides closure grooves crimping the top and bottom closure members to the cathode assembly, and thus provides the same function as corresponding grooves 102, 176, 178, 180, 122, 130, and the like, which provide closure seals on the previously described embodiments which use cathode cans. Thus, in the embodiments which use cathode cans, the top and bottom portions of the cathode can serve the same closure functions as the top and bottom closure members in the can-less embodiments. Accordingly, wherever herein we refer to a "top closure member" or a "bottom closure member," as respects closure and/or seal functions at the top and bottom of the cell, we specifically include respective top and bottom portions of the cathode can as the top and bottom closure members, in those embodiments which use a cathode can.

[0523] As an alternative to the tooling of FIGURE 35, in the embodiment of FIGURE 36, top closure member tool 234 advances downwardly onto channel 236, and pushes the entire cell assembly downwardly such that the respective outer leg 212 or 224, as appropriate, is crimped inwardly against tool 234 by conically-shaped receptacle tooling 238.

#### CAN-LESS CELL HAVING HOLLOW ANODE CURRENT COLLECTOR

[0524] The embodiments of FIGURES 37, 38, 39, and 39A take the invention yet another step further in improving the energy/weight ratio of the cell. In FIGURE 37, the bottom corner structure is generally as disclosed with respect to FIGURES 2 and 3A. At the top of the cell, grommet 18 includes an annular slot 240 which receives the top of the air cathode assembly. Top contour washer 206 is received on the top of grommet 18, and extends downwardly about the outer edge of grommet 18, crimping an outer flange 242 of the grommet, outwardly of slot 240, onto the cathode assembly, thus locking the cathode assembly into slot 240. A downwardly depending lip 244 of contoured washer 206



having a thickness, a top and a top edge, a bottom, a first outer surface and a first inner surface, and an array of perforations extending through the thickness of the side wall, from the outer surface of the side wall to the inner surface of the side wall; and

- 5 (b) a catalytically active carbon composition e.g. comprising carbon, polymeric binder and manganese (II) moieties, mounted on the side wall of said cathode current collector and extending into the perforations in said cathode current collector,

the resulting cathode assembly precursor having a second outer surface and a second inner surface.

- 10 2. A cathode assembly precursor according to Claim 1, said cathode current collector comprising a cylindrical cathode current collector free from longitudinal jointing along the length of said cathode current collector, or said cathode current collector comprising a longitudinally-extending joint free from overlap of elements of said side wall at said joint, or said cathode current collector comprising interdigitated elements of said side wall joined to each other and thereby forming a longitudinally-extending joint on said side wall.
- 15 3. A cathode assembly precursor according to Claim 1 or Claim 2, said cathode current collector comprising an imperforate edge region at at least one of said top and said bottom.
- 20 4. A cathode assembly precursor according to Claim 1, 2 or 3, said cathode current collector comprising imperforate edge regions at said top and said bottom, together extending along no more than 20 percent of the length of said cathode current collector, for example they together extend along about 5 percent to about 15 percent of the length of said cathode current collector.
- 25 5. A cathode assembly precursor according to any of Claims 1 to 4, the array of perforations defining a perforated area of said side wall, the array of perforations further defining an open fraction of said side wall, of about 45 percent to about 70 percent of the perforated area, preferably about 49 percent to about 65 percent of the perforated area.
- 30 6. A cathode assembly precursor according to any preceding Claim, respective ones of the perforations having perimeters defining corners therein, the corners being effective to assist in holding said carbon composition securely mounted to said cathode current collector.
- 35 7. A cathode assembly precursor according to any preceding Claim wherein said catalytically active carbon composition comprises a layer of said carbon composition disposed on one of the first inner and first outer surfaces of said cathode current collector, said composition either extending into the perforations, or said composition extending through the perforations to the other of the first inner and first outer surfaces of said cathode current collector, and extending laterally outwardly from respective ones of the perforations along the other of the first inner and first outer surfaces of said cathode current collector, and for example said catalytically active carbon composition covers substantially equal portions of the first inner and first outer surfaces of said cathode current collector.
- 40 8. A cathode assembly precursor according to any of Claims 1 to 6, wherein said catalytically active carbon composition covers substantially the entirety of each of the first inner and first outer surfaces of said cathode current collector.
- 45 9. A tubular cathode assembly comprising a cathode assembly precursor according to any preceding Claim, and including an air diffusion member mounted on the second outer surface of said cathode assembly precursor, said air diffusion member preferably having a thickness of about 0.0025 inch to about 0.005 inch.
- 50 10. A tubular cathode assembly according to Claim 9, said air diffusion member comprising an endless wrap of air diffusion sheet material extending at least 1.5 times, preferably at least 2 times and more preferably at least 3 times, about a circumference of the second outer surface of said cathode assembly precursor, such that said air diffusion member effectively discourages transfer of moisture vapor into or out of a cell into which said cathode assembly is incorporated, discourages leakage of liquid electrolyte, and controls rate of diffusion of air into the cell.
- 55 11. A tubular cathode assembly according to Claim 9, said air diffusion member comprising an endless wrap of air diffusion sheet material extending at least 2 times about a circumference of the second outer surface of said cathode assembly precursor, the air diffusion sheet material having variations in thickness along the length of said air diffusion sheet material, of at least 5 percent, the at least two wraps attenuating the effect of the variations in

the mandrel and the cathode current collector in a stack of assembly rolls;

(c) fabricating carbon sheet structure comprising catalytically active carbon, and up to about 10 percent by weight of a binder, and thereby forming sheet structure of the catalytically active carbon composition, having a machine direction and a cross direction;

(d) making a sheet stack of respective overlying underlying ones of at least first and second elements of the carbon sheet structure, such that the sheet stack has a top and a bottom, and a thickness therebetween;

(e) passing the sheet stack through a nip and thereby applying force to the stack such that the applied force effects reduction in the thickness of the stack, in combination with consolidation of the respective elements of the carbon sheet structure into a unitary composite carbon sheet; and

(f) passing the so-consolidated carbon sheet into the stack of assembly rolls and thus through at least one nip acting between the mandrel/current collector and a respective one of the assembly rolls, and applying force at the at least one nip sufficient to collectively apply and consolidate the consolidated carbon sheet onto an outer surface of the elongate side wall of the cathode current collector; and

for example in step (f) sufficient force is applied at the at least one nip to deform portions of the carbon sheet into the perforations, thereby mechanically securing the carbon sheet to the cathode current collector.

20. A method according to Claim 19, including, after consolidating the carbon sheet onto the cathode current collector, while retaining the assemblage of the cathode current collector and the carbon sheet on the mandrel, passing an air diffusion material into the stack of assembly rolls and thus through the at least one nip, and applying force at the at least one nip collectively sufficient to apply and consolidate the diffusion material onto the carbon sheet, and optionally (a) including compressing or stretching the air diffusion material while passing the air diffusion material into the stack of assembly rolls and thus through the at least one nip, applying a sufficient length of such compressed or stretched air diffusion material to the carbon sheet to wrap the carbon sheet in at least two and preferably at least three endless layers of compressed or stretched air diffusion material, thereby to fabricate onto the carbon sheet a unitary, multiple layer air diffusion member; and/or (b) including aligning the air diffusion material so as to extend outwardly beyond an edge of the cathode current collector, and folding the outwardly extending portion inwardly about the edge of the cathode current collector and against an inner surface of the cathode current collector.

21. A method according to Claim 19 or Claim 20, including applying liquidous seal rings on the air diffusion member adjacent opposing ends of the cathode current collector.

22. An air depolarized electrochemical cell comprising an anode, a cathode, a separator, and electrolyte, said cathode comprising a tubular cathode assembly comprising a cathode assembly precursor according to any of Claims 1 to 8, or a cathode assembly according to any of Claims 9 to 13.

23. An air depolarized electrochemical cell comprising an anode, a cathode, a separator, and electrolyte, said cathode comprising a tubular cathode assembly made according to a method according to any of Claims 14 to 21.

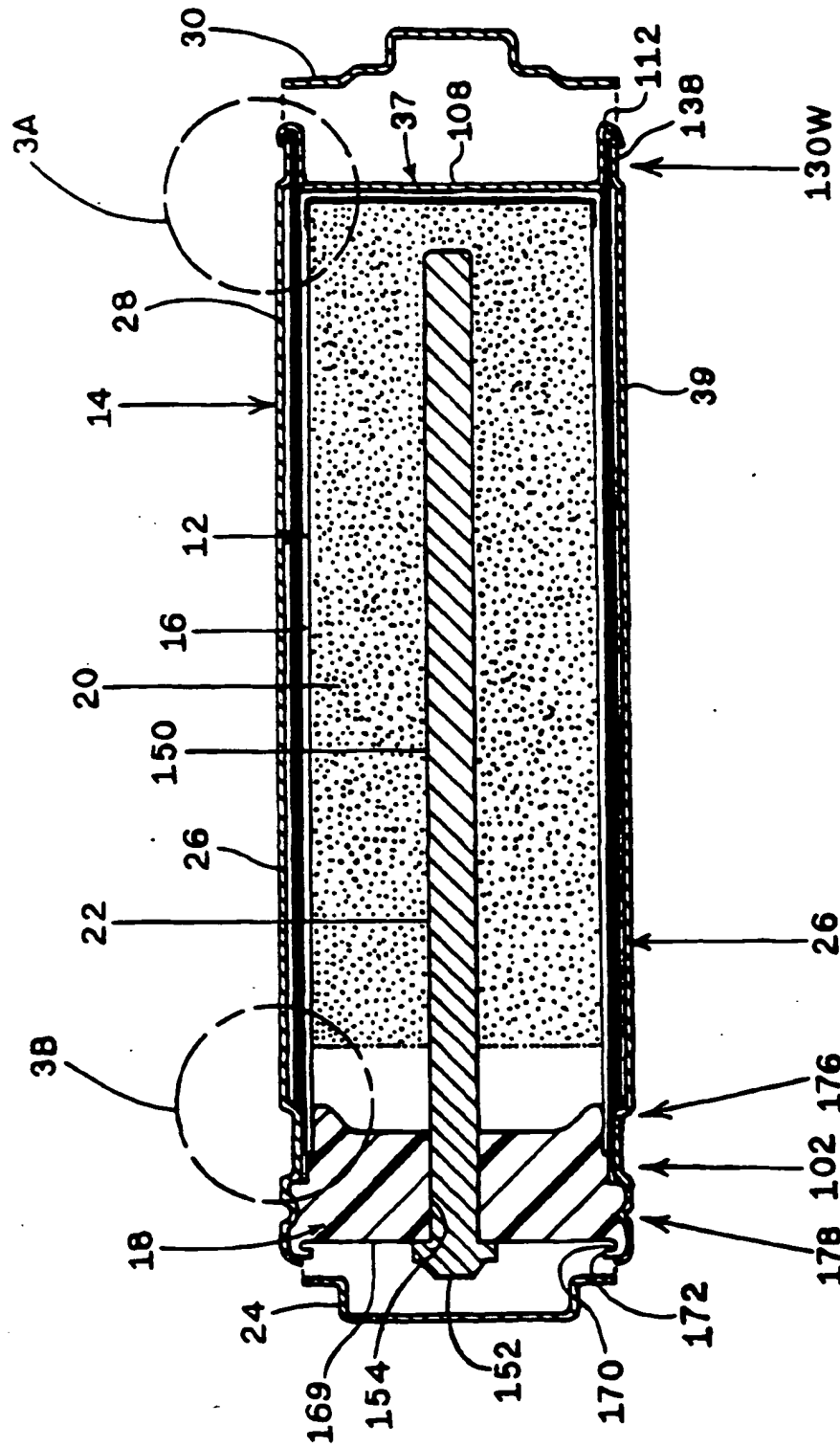


FIG. 2

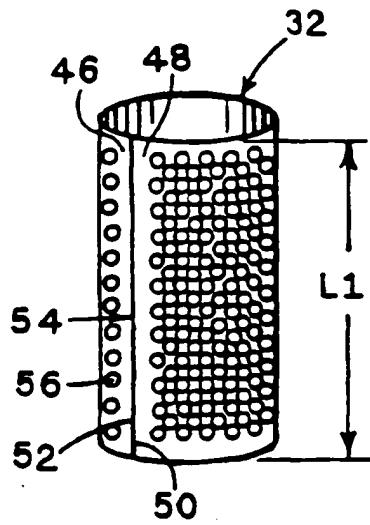


FIG. 4

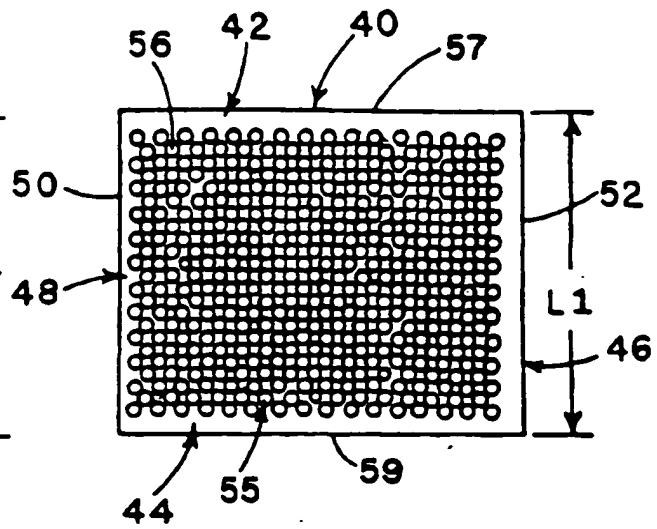


FIG. 5

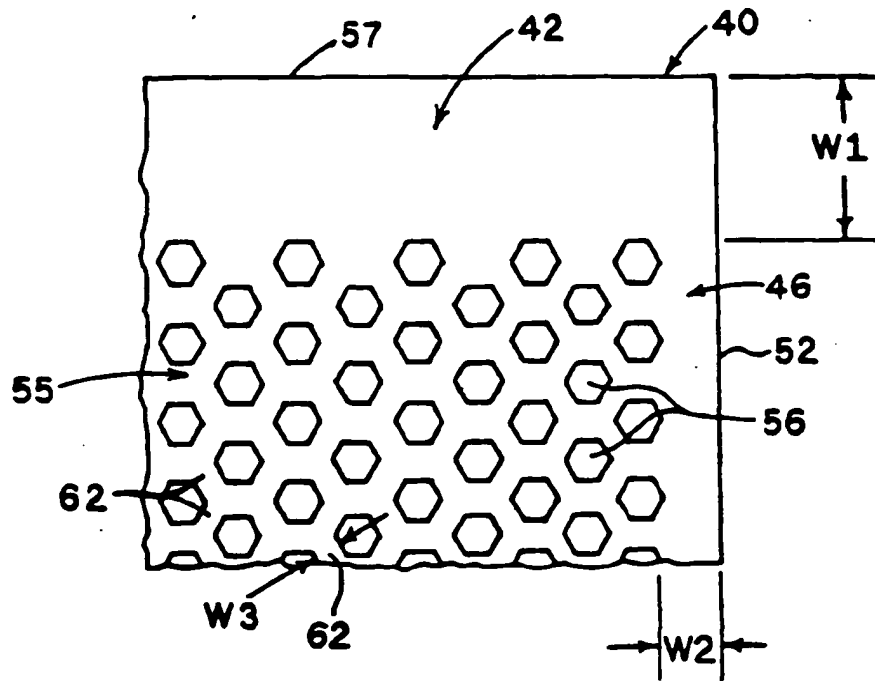


FIG. 6

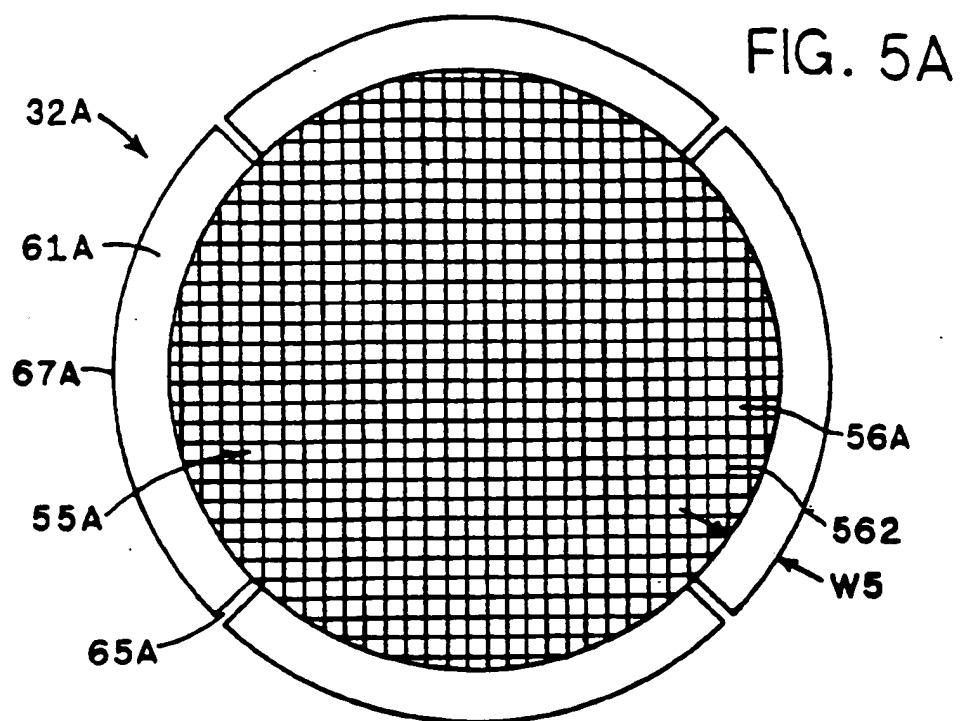


FIG. 5B

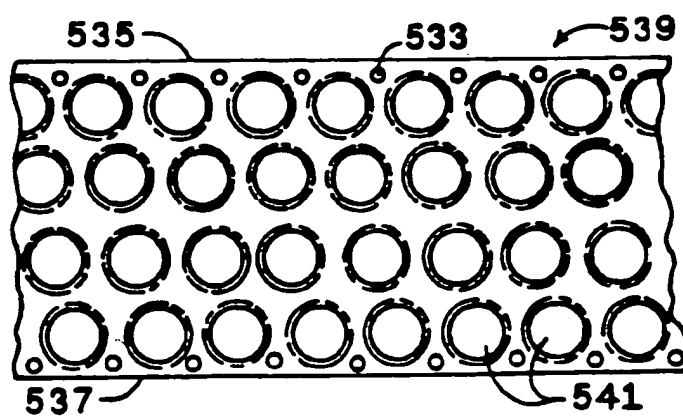


FIG. 5C

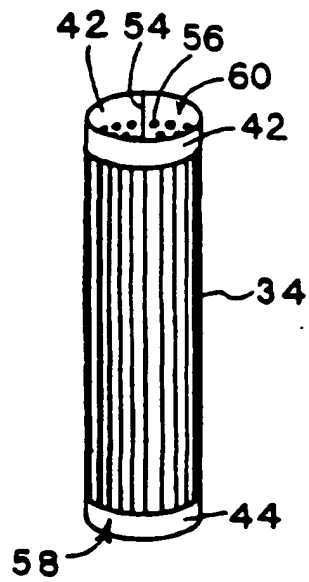


FIG. 10

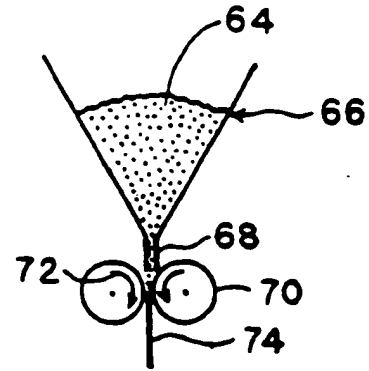


FIG. 11

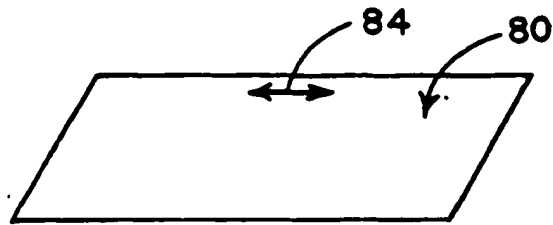


FIG. 12

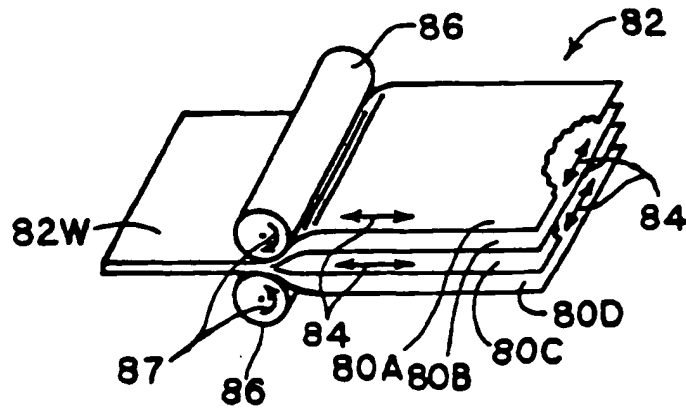


FIG. 12A

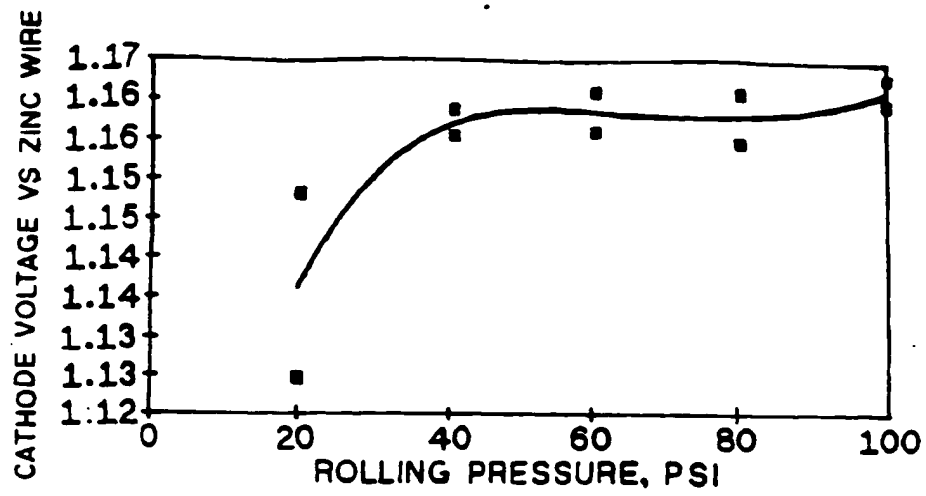


FIG. 15

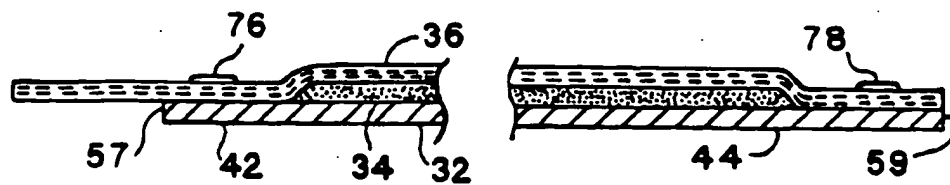


FIG. 16

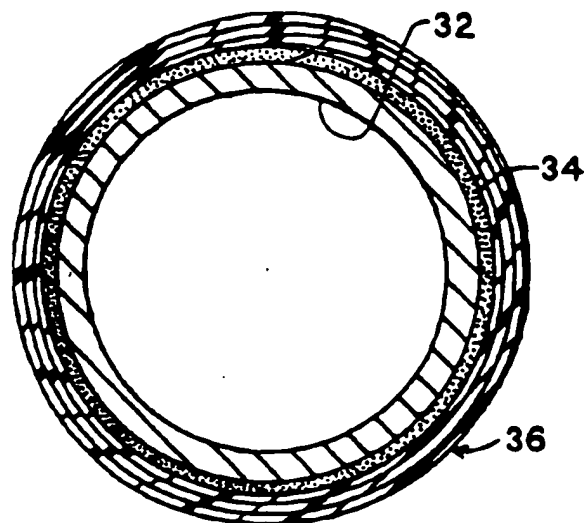


FIG. 17

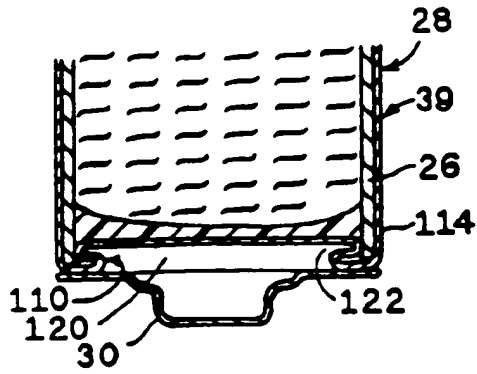


FIG. 21

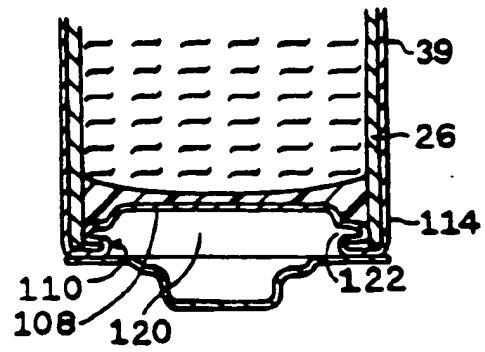


FIG. 22

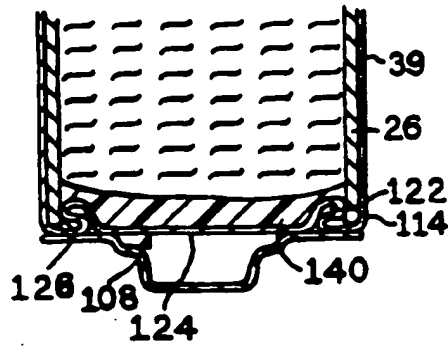


FIG. 23

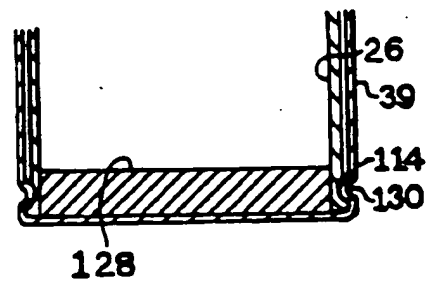


FIG. 24



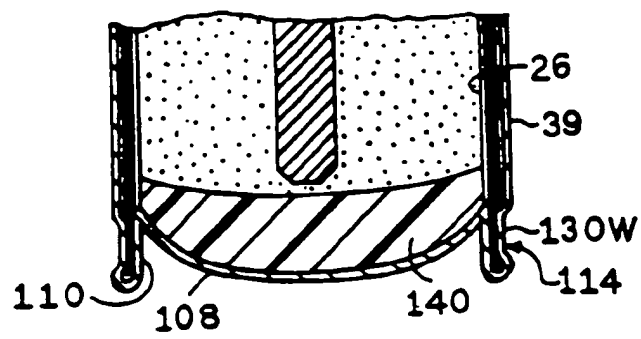


FIG. 27

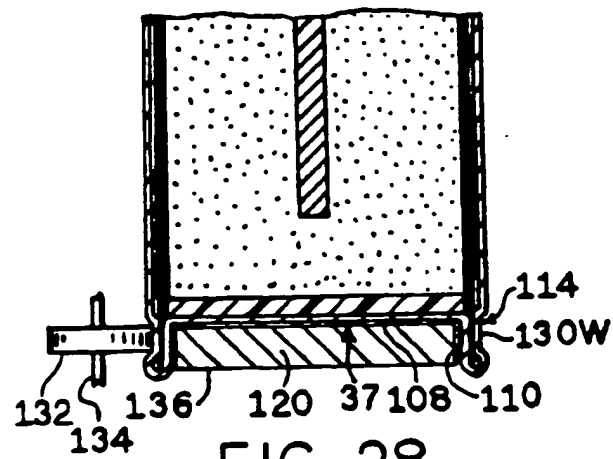


FIG. 28

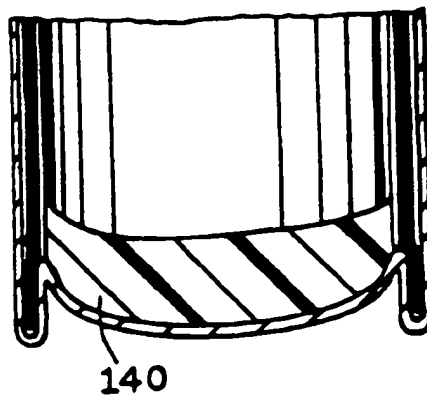


FIG. 29

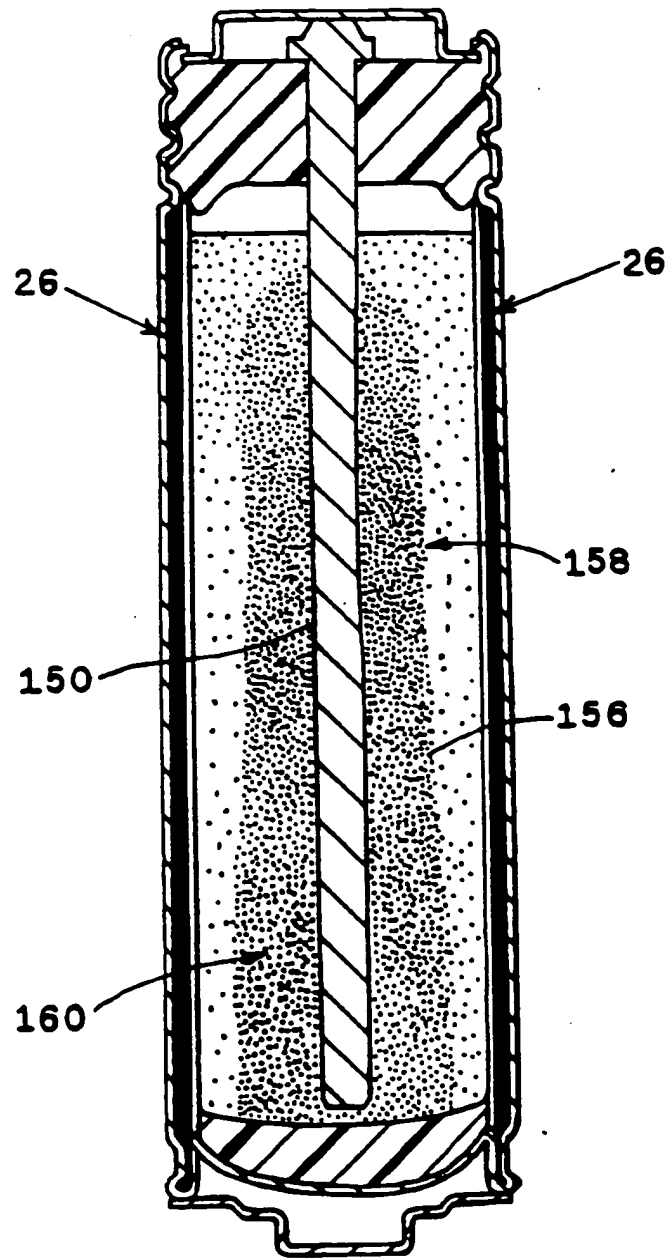


FIG. 31A

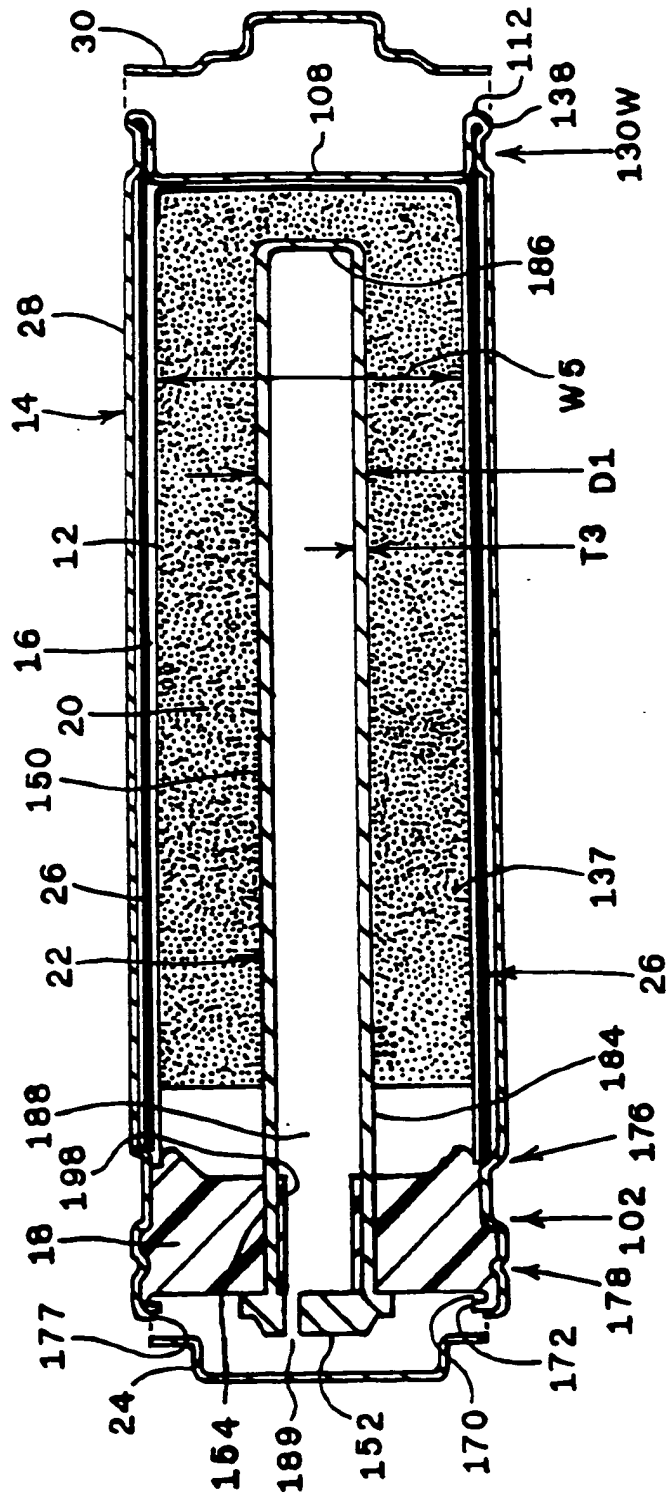


FIG. 32

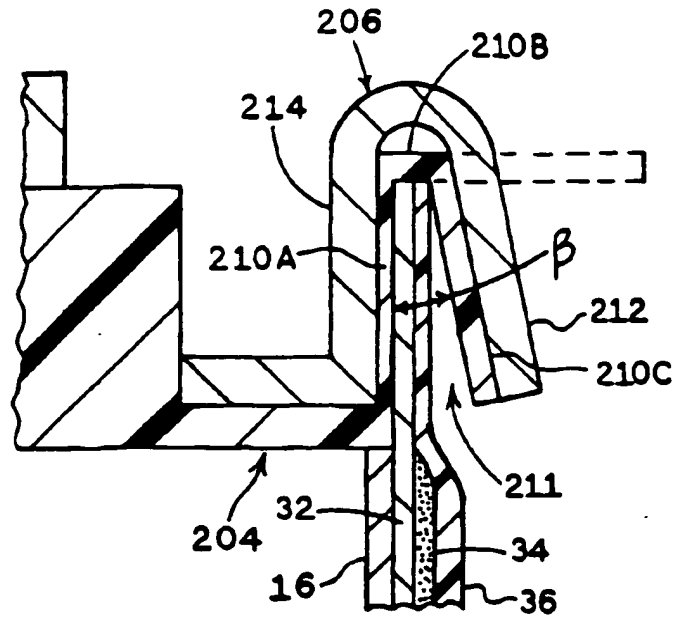


FIG. 34A

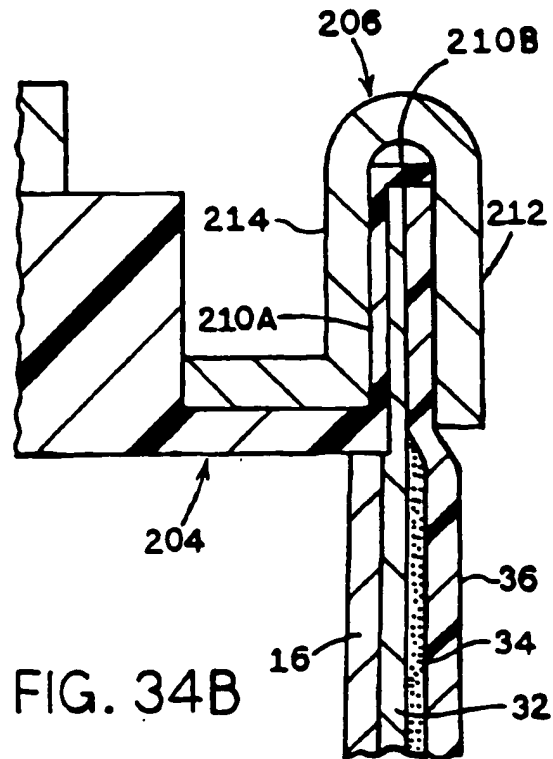


FIG. 34B

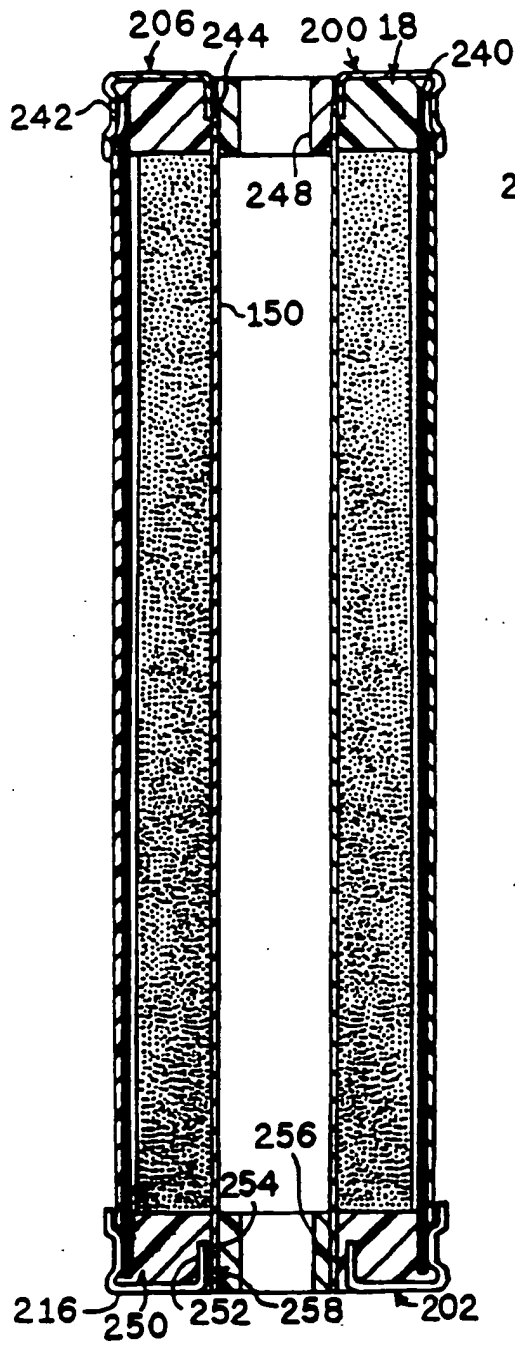


FIG. 38

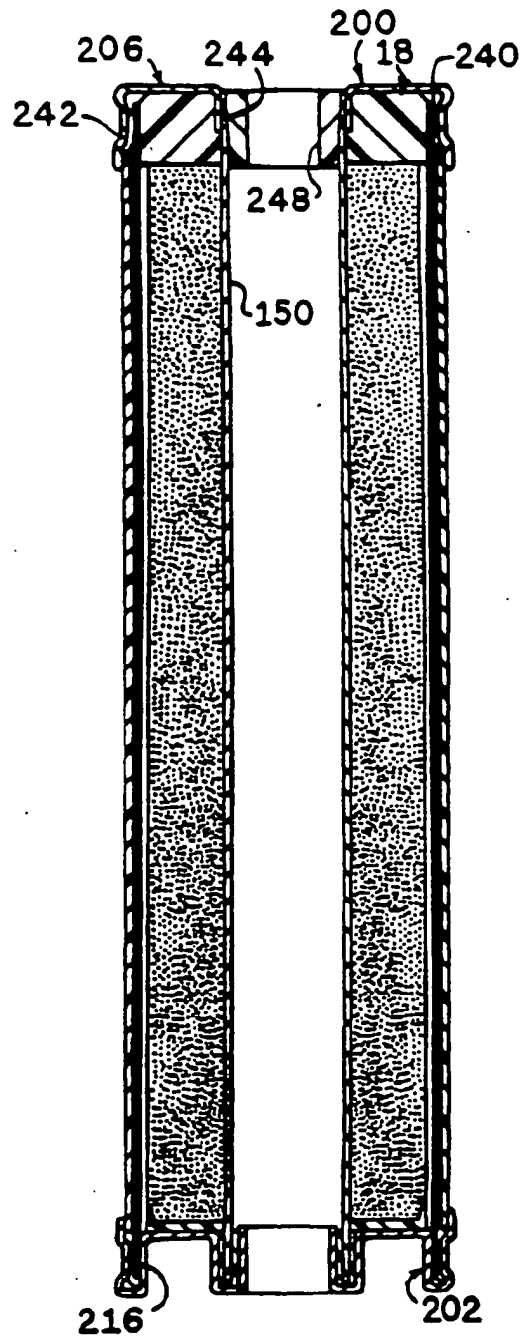


FIG. 39

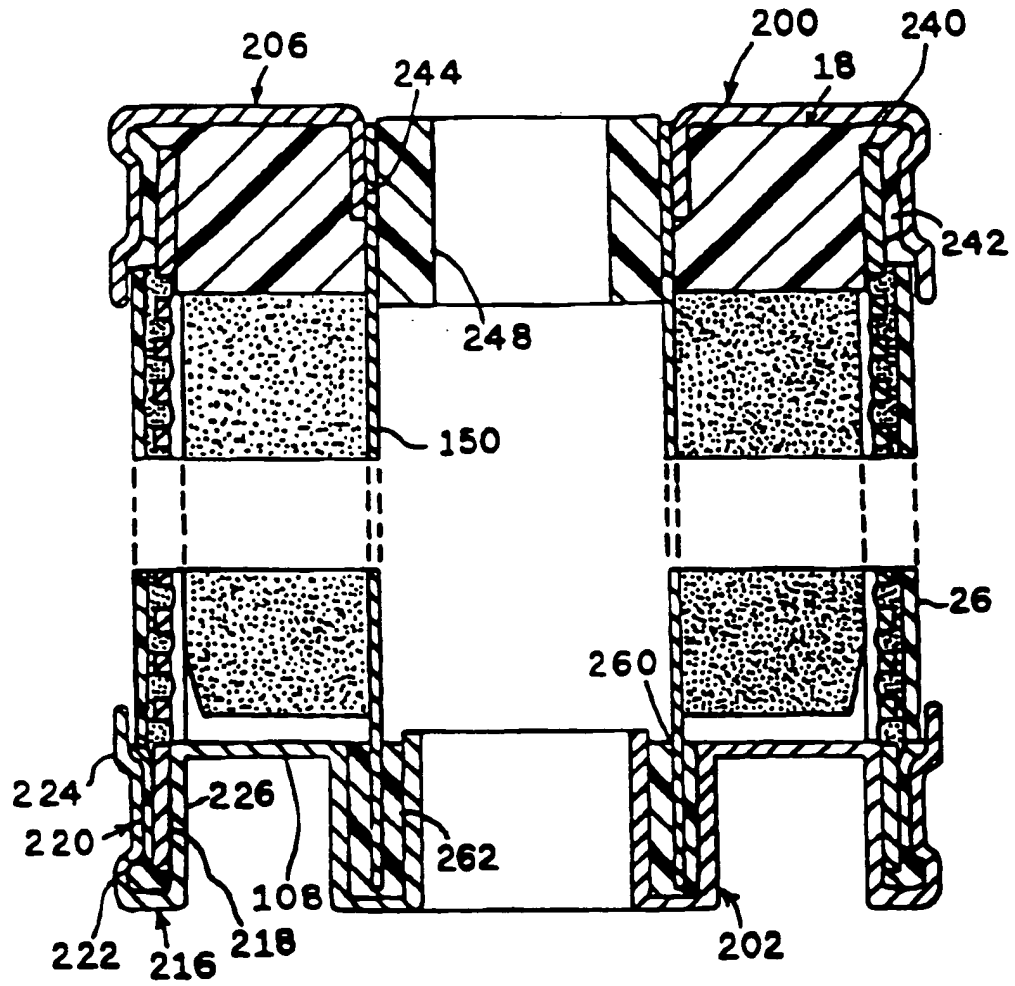


FIG. 39A